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=> s container or bottle

=> s 11 and 12

L3 1348 L1 AND L2

=> s continuous film

518990 CONTINUOUS
1 CONTINUOUSES
518991 CONTINUOUS
(CONTINUOUS OR CONTINUOUSES)

320102 FILM
128890 FILMS
340791 FILM
(FILM OR FILMS)

L4 6570 CONTINUOUS FILM
(CONTINUOUS (W) FILM)

=> s 13 and 14

L5 27 L3 AND L4

=> focus

PROCESSING COMPLETED FOR L5
L6 27 FOCUS L5 1-

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1. 5,693,283, Dec. 2, 1997, **Container** with recycled plastic; Gregory M. Fehn, 264/513; 215/12.1; 264/512, 515, 918; 428/36.6, 36.7 [IMAGE AVAILABLE]

=> d 2-

2. 4,810,542, Mar. 7, 1989, Multilayered tube for draw molding and multilayered **container** utilizing the tube; Syuji Kawai, et al., 428/36.7; 264/512, 515; 428/36.91, 213, 480, 483, 522, 542.8 [IMAGE AVAILABLE]

3. 4,534,930, Aug. 13, 1985, Process for producing stretched multilayer polyester **bottle**; Shigezo Nohara, 264/513, 520, 521 [IMAGE AVAILABLE]

4. 4,515,836, May 7, 1985, Process for coating substrates with aqueous polymer dispersions; Walter H. Cobbs, Jr., et al., 427/425; 215/12.2; 427/421; 428/36.7, 483 [IMAGE AVAILABLE]

5. 4,573,429, Mar. 4, 1986, Process for coating substrates with aqueous polymer dispersions; Walter H. Cobbs, Jr., et al., 118/322, 320, 326 [IMAGE AVAILABLE]

6. 5,492,953, Feb. 20, 1996, Resin composition; Sumio Itamura, et al., 524/239, 242, 427, 436, 449, 451, 503, 528; 525/60, 61, 240 [IMAGE AVAILABLE]

7. 5,389,709, Feb. 14, 1995, Resin composition; Sumio Itamura, et al., 524/239, 242, 427, 436, 449, 451, 503, 528; 525/60, 61, 240 [IMAGE AVAILABLE]

8. 5,196,469, Mar. 23, 1993, **Ethylene/vinyl alcohol** coatings; Virginia P. Cushing, et al., 524/300; 427/407.1, 411, 412.5; 524/321, 389, 522 [IMAGE AVAILABLE]

9. 4,771,935, Sep. 20, 1988, Plastic **containers** embodying a peel seal and method of preparing same; Ihab M. Hekal, 229/3.5R; 156/334; 206/484.2; 229/123.1, 125.35 [IMAGE AVAILABLE]

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11. 5,498,478, Mar. 12, 1996, **Polyethylene** glycol as a binder material for fibers; Michael R. Hansen, et al., 428/372, 357, 359, 375, 393; 442/417 [IMAGE AVAILABLE]

12. 5,096,738, Mar. 17, 1992, Siloxane polymers and copolymers as barrier, coatings and method of producing barrier coating properties therewith; John E. Wyman, 427/503, 387, 393.4, 393.5; 428/339, 447, 451 [IMAGE AVAILABLE]

13. 5,175,035, Dec. 29, 1992, Multilayer sheet with one layer easily peelable from another; Francis Pinsolle, et al., 428/35.7, 349, 516, 523 [IMAGE AVAILABLE]

14. 5,432,000, Jul. 11, 1995, Binder coated discontinuous fibers with adhered particulate materials; Richard H. Young, Sr., et al., 428/372, 357, 361, 373, 375, 378, 393 [IMAGE AVAILABLE]

15. 4,225,650, Sep. 30, 1980, Crosslinkable polymer powder and laminate; Robert A. van Brederode, et al., 428/405, 407, 429, 447; 525/342, 387 [IMAGE AVAILABLE]

16. 5,701,724, Dec. 30, 1997, Method and apparatus for forming and hermetically sealing slices of food items; Vincent A. Meli, et al., 53/451, 122, 374.5, 477, 551; 426/130, 414 [IMAGE AVAILABLE]

17. 5,667,071, Sep. 16, 1997, Photosensitive material package and packaging apparatus for the same; Isao Nakagoshi, et al., 206/455, 389, 471, 497; 428/34.9 [IMAGE AVAILABLE]

18. 5,440,860, Aug. 15, 1995, Method and apparatus for forming and hermetically sealing slices of food items; Vincent Meli, et al., 53/451, 122, 374.5, 477, 551; 426/130, 414 [IMAGE AVAILABLE]

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21. 5,102,733, Apr. 7, 1992, Repulpable pressure-sensitive adhesive constructions; Mary E. Zawadzki, 428/343; 162/4; 428/211, 355AC, 355BL [IMAGE AVAILABLE]

22. 5,619,844, Apr. 15, 1997, Method and apparatus for forming a slice of a food item having a heat tacks seal; Vincent A. Meli, et al., 53/550, 371.4, 371.5, 374.3, 374.4; 99/453; 426/410, 414 [IMAGE AVAILABLE]

23. 5,516,585, May 14, 1996, Coated fiber product with adhered super absorbent particles; Richard H. Young, Sr., et al., 428/372, 357, 361, 373, 375, 378, 393; 442/330 [IMAGE AVAILABLE]

24. 5,347,792, Sep. 20, 1994, Method and apparatus for forming a slice of a food item having a heat tack seal; Vincent A. Meli, et al., 53/450, 371.4, 371.5, 374.3, 374.4, 479, 550; 99/453; 426/130, 410, 414 [IMAGE AVAILABLE]

25. 5,230,959, Jul. 27, 1993, Coated fiber product with adhered super absorbent particles; Richard H. Young, Sr., et al., 428/372, 359, 361, 373, 375, 378, 393 [IMAGE AVAILABLE]

26. 5,064,689, Nov. 12, 1991, Method of treating discontinuous fibers; Richard H. Young, Sr., et al., 427/202; 156/62.2; 264/121, 122, 123; 425/83.1 [IMAGE AVAILABLE]

27. 5,057,166, Oct. 15, 1991, Method of treating discontinuous fibers; Richard H. Young, Sr., et al., 156/62.2; 19/305; 156/62.6, 166, 181; 264/121; 425/80.1 [IMAGE AVAILABLE]

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US PAT NO: 4,810,542 [IMAGE AVAILABLE] L6: 2 of 27

ABSTRACT:

The tube of the present invention has no or very small local minute nonuniformity in thickness of **EVOH** layer, and therefore drawn-formed articles such as blow **bottle** obtained by draw molding the tube have no streaks and are superior in appearance.

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US PAT NO: 4,810,542 [IMAGE AVAILABLE] L6: 2 of 27

TITLE: Multilayered tube for draw molding and multilayered **container** utilizing the tube

ABSTRACT:

The tube of the present invention has no or very small local minute nonuniformity in thickness of **EVOH** layer, and therefore drawn-formed articles such as blow **bottle** obtained by draw molding the tube have no streaks and are superior in appearance.

SUMMARY:

BSUM(3)

The present invention relates to a multilayered tube comprising a saturated polyester (hereinafter referred to as **PES**) as the inner and the outer layers, a saponified product of ethylene-vinyl acetate copolymer (hereinafter referred to as **EVOH**) as the intermediate layer, and an adhesive resin (hereinafter referred to as **TR**) layer between the **PES** layer and the **EVOH** layer; and a multilayered **container** utilizing the tube; as well as methods of producing the tube and the **container**.

SUMMARY:

BSUM(5)

PES, represented by **Polyethylene** terephthalate (hereinafter referred to as **PET**) is, because of its high transparency, heat resistance, mechanical properties, and so on, widely used not only for fibers and films but for **containers** for beverages and foods or as films for food packaging. In the case where **PES** is used for **containers** for foods or films for food packaging, though it has by itself a certain degree of gas barrier property and. . . on the type of foods or beverages to be filled or packed therein. Thereupon, attempts have been made to have **EVOH**, which resin has a higher gas barrier property, laminate onto **PES** to obtain tubes, blow **bottles** and films having multilayered structures. For example, JPA's Nos.

108162/1978, 77144/1981, 128516, 1982, U.S. Pat. No. 4,504,531, and JPA No. 199237/1984 disclose tubes and blow **bottles** which have laminated the two resins. However, when a composite of **PES** and **EV OH** is formed into a biaxially drawn multilayered **container**, there is observed in the appearance of the **container** (bottle) an abnormal nonuniformity looking like streaks to make the **bottle** unsatisfactory. FIG. 10 is an elevation of a **bottle** of bad appearance, showing streaky nonuniformities. This streakiness, S (hereinafter referred to simply as streaks), markedly deteriorates the commercial value of the **bottle**, and the **bottle** can not stand comparison with monolayered **bottles** of PET which are sold commercially.

SUMMARY:

BSUM(7)

The present inventors thought that such streaks of the blow **bottles** can not fully be eliminated by improving uniformities in thickness of the tube or of **EV OH** layer or each layer, and that the streaks are caused by poor drawability of **EV OH** used as a gas barrier resin, and have carried out a series of studies centering on improving blow molding conditions. . . . limit in improvements by blow conditions or by various manufacturing conditions, and it has been difficult to get the desired **bottle** having no streaks.

SUMMARY:

BSUM(8)

The . . . unexpectedly that the fundamental factor of causing streaks is the local minute nonuniformity in thickness of a small region of **EV OH** layer in the tube, in other words such local minute nonuniformity in thickness governs the streak. In more detail, there was found that the local minute roughness of **EV OH** layer in the tube causes, in the course of biaxial draw blowing, bigger irregularities in the **EV OH** layer and **bottle** wall thickness. The local minute nonuniformity in thickness generates continuously when a tube is molded, along the flow at the. . . .

DRAWING DESC:

DRWD(2)

FIG. 1 shows a circumferential distribution of thickness of **EV OH** layer in the cross section of **bottle** body (point A: maximum thickness (t_{max}); point B: minimum thickness (t_{min}); distance between t_{max} and t_{min} (L)), wherein the abscissa represents circumferential distance and the ordinate represents thickness of **EV OH** layer.

DRAWING DESC:

DRWD(3)

FIG. 2 shows a diagrammatical drawing showing local minute nonuniformity in the thickness of the **EV OH** layer (E_{max} and E_{min} are the maximum thickness and the minimum thickness respectively between points P._{sub.n} and P._{sub.n+1} which is. . . .

DRAWING DESC:

DRWD(5)

FIG. 4 is a perspective view of the **EV OH** layer only of the tube.

DRAWING DESC:

DRWD(9)

FIG. 9 is an elevation of the biaxially drawn blow **bottle** having no streaks obtained from the tube of Example 1.

DRAWING DESC:

DRWD(10)

FIG. 10 is an elevation of the biaxially drawn blow **bottle** having streaks obtained from the tube of Comparative Example 1.

DRAWING DESC:

DRWD(11)

FIG. 11 shows the thickness distribution of the **EVOH** layer of the **bottle** prepared in Example 1.

DRAWING DESC:

DRWD(12)

FIG. 12 shows the thickness distribution of the **EVOH** layer of the **bottle** prepared in Comparative Example 1, wherein the abscissa represents the circumferential distance in the cross section and the ordinate represents. . .

DRAWING DESC:

DRWD(13)

FIG. . . . die used in manufacturing the tube according to the present invention when TR is introduced; and (2) when TR and **EVOH** are introduced.

DETDESC:

DET D(2)

What is essential in the present invention is that the **EVOH** layer as the intermediate layer of a multilayered tube satisfy the above equation II, that is, to eliminate in minute regions any local nonuniformity in thickness. ##EQU3## greatly influences streaks in **bottles** and when Y exceeds ##EQU4## the local minute nonuniformity in thickness becomes greater, which as the **EVOH** layer is drawn will cause nonuniformity in the drawing behavior to cause streaks to generate.

DETDESC:

DET D(3)

The . . . and molding tests and found out as a result therefrom that, for the purpose of obtaining a biaxially drawn blow **bottle** of 3-kind/5-layer of **PES/TR/EVOH/TR/PES** having substantially no irregular streaky defects in appearance, i.e. streaks, it is not effective to simply improve structure of the multilayered tube such as thickness control of the **EVOH** layer and eliminate thickness irregularity of TR layer; but it is necessary to eliminate local minute variation in thickness of the **EVOH** layer in the tube, that is, the condition (II) must be fulfilled. The problem of streaks generation caused by poor drawability of **EVOH** is usually not applicable to other multilayered structures comprising **PES**, **polyethylene**, **polypropylene**, **nylon**, etc., and not containing **EVOH**.

DETDESC:

DETD(4)

In case of all PET **bottles** or all PET multilayered **bottles**, such minute local variation in thickness will, thanks to a very high drawability of PET resin, not promote thickness nonuniformity of the PET layer causing no streaks to form. However, since **EVOH** resin is, compared with PET resin, very poor in drawability, particularly in uniform drawability, even a small variation in thickness. . . extent while thick portions remain to be drawn at a low ratio, which in turn remain as nonuniformities in the **EVOH** layer, and further as big irregularities in thickness of the **bottle**. Because such a minute nonuniformity in thickness is the nonuniformity of flow which generates continuously in the course of tube molding and generates continuously in the direction of tube flow (machine direction), it remains enlarged on the **bottle** body as a streaky thickness irregularity which extends continuously in the machine direction. This poorly drawn irregularity of **EVOH** layer influences the drawing of TR layer and PET layer; and a big variation, i.e. poorly drawn portions in **EVOH** layer will, causing poor drawability of TR and PET layers, remain enlarged in the whole wall of the **bottle**, which makes bigger nonuniformity in light refractivity resulting in a streaky appearance i.e. streaks.

DETDESC:

DETD(5)

In the present invention, to satisfy substantially the above condition II means that all or almost all of spots in the **EVOH** layer in the cross section of the tube satisfy the condition II, whereas such minute local thickness irregularities (not satisfying. . . the conditon II, since the spots will form a streak upon drawing. Only one spot of the above two in **EVOH** layer not satisfying the condition II may sometimes not cause a streak.

DETDESC:

DETD(8)

In a multilayered tube having $H \approx 30$ mm and a thickness of **EVOH** layer of $E = 300 \mu$, the allowable range for the irregularity is 210 to 390μ . calculated from the inequality $I - \circlearrowleft \approx 2 \dots$

DETDESC:

DETD(10)

Suppose . . . satisfies the condition of local minute thickness nonuniformity: ##EQU5## that is, satisfies $E_{max} - E_{min} \approx 9 \mu$, so that the biaxially drawn blow **bottles** obtained from the tube do not form any streaks.

DETDESC:

DETD(11)

However, in contrast with the above, for instance in the case of an **EVOH** layer and a remarkable uniform thickness having a total thickness range of 290μ to 310μ , which range is far below. . . each other exceeds the allowable limit of Condition II: $(E_{max} - E_{min}) \approx 9 \mu$, e.g. with $Q = 500$ and $(E_{max} - E_{min}) = 10 \mu$, the biaxially drawn blow **bottles** obtained from the tube will have streaks and bad appearances. Further in the case where the thickness difference between two. . .

DETDESC:

DET D(12)

The above facts show that the allowable range of local minute thickness nonuniformity of an **EVOH** layer varies greatly depending on the size of the corresponding local minute segment. Though drawing behavior is not completely understood, . . . local portions probably have a strong influence on that behavior among other factors relative to the wall thickness of the **EVOH** layer.

DETDESC:

DET D(13)

FIG. . . . the cross section of the tube according to the present invention showing local minute nonuniformity in the thickness of the **EVOH** layer.

DETDESC:

DET D(15)

The . . . about $Q=500.\mu$. and checking the gradient will be effective in practice, especially for process control and the like. Accordingly, for **EVOH** layer of a multilayered tube molded at a steady rate, those local thickness irregularities observed in a region $Q<100.\mu$. are. . .

DETDESC:

DET D(17)

Measurement of the total range of thickness and local minute thickness nonuniformities is done on **EVOH** layer following the procedures below.

DETDESC:

DET D(22)

Though TR layer and **EVOH** are relatively transparent, the boundary lines can be seen from differences in refractivity and color shade to make possible measurement. . .

DETDESC:

DET D(23)

The present inventors have also studied how to take out **EVOH** layer without damaging it from a multilayered tube, and have found an effective method to measure the thickness, thus making it possible to have the **EVOH** layer only be observed with the naked eye or with a special microscope as well as subjected to measurement with. . . a thickness tester. That is, in the case where the softening point of TR layer is lower than those of **PES** and **EVOH**, the following method is effective as well as simple and easy.

DETDESC:

DET D(24)

(1) Heat a sliced multilayered tube in a heating furnace, etc., to a temperature below melting points of **PES** resin and **EVOH** resin, and above that of TR resin, to soften TR layer

DETDESC:

DET D(25)

(2) Take out **EVOH** layer by sliding **PES** layer and **EVOH** layer in the longitudinal direction,

DETDESC:

DET_D(26)

(3) Peel off adhering TR layer by using as required, a special delamination solvent having mixed acetone, etc. to obtain spotless **EVOH** layer, and

DETDESC:

DET_D(27)

(4) Serve the **EVOH** layer for a measurement by clear observation.

DETDESC:

DET_D(28)

FIG. 4 shows a perspective view of **EVOH** layer obtained from the tube. Most simply, the thus obtained **EVOH** layer is held to the light to allow a full observation of local minute nonuniformities C (cavity) and D (projection). . . .

DETDESC:

DET_D(31)

I-.circle.1 specifies the range of thickness of **EVOH** layer. Though as **EVOH** layer is made thinner more uniformly the layer is drawn to form less streaks, an improvement in the barrier property which should be the top object of having multilayer can not be achieved if the **EVOH** layer is made too thin. Further, in the case where the **EVOH** layer in a tube is as thin as less than 50. μ ., it is very difficult to maintain a continuous molding for a long time of a multilayered tube having uniform **EVOH** layer of small thickness biases. Consequently, the thickness should be 50. μ . or above, preferably 150. μ . or above. On the other hand, as **EVOH** layer is made thicker, a poor drawability of **EVOH** becoming an issue, irregularities upon drawing will increase to make streaks highlighted as well as to worsen the cooling of. . . . the thickness be not more than 1000. μ . and more preferably: 150. μ .ltoreq.E.ltoreq.700. μ .. From the viewpoint of gas barrier property required for **bottles** for general refreshing drinks in the market also, it is said that a thickness of 700. μ . (about 50. μ . after drawing). . . .

DETDESC:

DET_D(32)

I-.circle.2 is an allowable variation in the thickness of **EVOH** layer. Prevention of biased thickness of **EVOH** layer is very difficult because of poor flow characteristics of **EVOH**. However since such biased thickness directly cause nonuniformity of drawing and generation of streaks, a variety of studies have been. . . .

DETDESC:

DET_D(33)

I-.circle.3 refers to a ratio of **EVOH** layer to **PES** layers. It is, though not deemed so important a factor in a general multilayered tube, an important condition for obtaining a streakless **bottle** by uniformly drawing a multilayered tube containing an **EVOH** layer.

PES layers have a important function of helping uniformly draw **EVOH** which is by itself of poor drawability, by co-drawing. In the case where the ratio of **PES** layers is small, the **PES** layers themselves being affected by poor drawability of **EVOH** layer, the whole **bottle** will undergo nonuniform drawing resulting in greater irregularities in thickness, which will make it difficult to eliminate streaks. For this. . . .

DETDESC:

DETD(61)

IV- . . . where a high-thickness molding is difficult to carry out, there are restrictions on the caliber and body diameter of the **bottle** from limitation in the drawing ratio of the body, and the ratio (surface area of **bottle**)/(volume of **bottle**) will increase to adversely affect the barrier effect. Therefore, preferred is 15 mm or higher. For a multilayered tube having. . . . to a minimum required drawing ratio, which requires higher pressure resistance and makes necessary a thicker wall, a restriction on **bottle** caliber by tube diameter, and that preparation of preforms is difficult.

DETDESC:

DETD(62)

IV- . . . demounting from the mold, at blow molding: nonuniform heating to cause not only deformation and irregularity in thickness of the **bottle**, but also thereby an increase of streaks on the **bottle**, so that it is required that the tolerance of the outer diameter be $+.-.2\%$ or below, preferably $+.-.1\%$ or below.

DETDESC:

DETD(63)

IV- . . . molding on account of irregular thickness, deformation of the tube, and the like. Moreover in such a case, as pressure **bottle** where in general a drawing ratio of 5 to 15 times is applied, the wall thickness becomes thin and so liable to deform or damage by an external force to make the **bottle** unsuitable for use. On the other hand a thick wall of 7000 .mu. or thicker will worsen the heat transfer, and cause whitening phenomena to occur at portions of **EVOH** layer of **PES** layer due to crystallization, thus rendering it difficult to obtain a **bottle** having a transparent feeling. A more preferred range is 1500.mu..1toreq.Z.1toreq.6000.mu..

DETDESC:

DETD(64)

IV- . . . will maintain and enlarge the bias as thick biased wall portions. These portions will cause deformation of tube, deformation of **bottle**, poor strength, poor barrier property, etc., which do not give a satisfying **bottle**. Besides, the nonuniformity in drawing will help increase streaks, and also, the biased thickness of whole wall affects the quality. . . .

DETDESC:

DETD(65)

IV- .circle.5 specifies the range of wall thickness of the inner **PES** layer. In the case where the wall thickness of the inner layer is 300 .mu. or below, not only molding of the tube becomes difficult; but since **EVOH** layer is placed closer to the inside of the **bottle**,

when used as a **bottle** for water-related beverages such as beverages containing carbon dioxide gas, water content of **EVOH** becomes higher to markedly decrease the barrier property resulting in an insufficiency in the barrier property. Besides, an inward shift of **EVOH** layer by a thinner inner layer will worsen the external cooling effect at the time of sizing cooling of the. . . thin an inner layer, thus making it difficult preparation of a good preform. Therefore, the wall thickness of the inner **PES** layer is preferably 300.mu. or above, more preferably 500.mu. or above. On the other hand, a too thick wall of. . . as an increase in the solubility of carbon dioxide gas contained in a carbon dioxide gas beverage into the inner **PES** layer, worsening of resistance to pressure against internal pressure of the gas, which in turn causes delamination at the adhesive resin layer to occur, and so on. Therefore, the wall thickness of the inner **PES** layer is not more than 5000 .mu., more preferably not more than 4000.mu..

DETDESC:

DETD(66)

IV- .circle.6 specifies tolerances for the thickness of the inner **PES** layer. Since too high a variation causes nonuniformity in gas barrier property, and since a good balance is required for. . .

DETDESC:

DETD(67)

IV- .circle.7 specifies the range of the thickness of the outer **PES** layer. Though molding of a thinner outer, than inner layer is possible, still it is still difficult to mold 150.mu. or below. Further, too thin an outer **PES** layer will, in the case of a pressure **bottle** such as the one for carbonate beverages, produce a problem of delamination in the intermediate **EVOH** layer caused by stress which generates in the adhesive resin layer. On the other hand, a construction comprising a **PES** layer of more than 4000.mu. thick will, though the molding is possible, shift **EVOH** layer inwardly, that is, to a high-moisture side resulting in worsening of barrier effect and external cooling effect of the **EVOH** layer.

DETDESC:

DETD(68)

IV- .circle.8 specifies tolerances for the wall thickness of the outer **PES** layer to be .+- .25%, more preferably .+- .20%, settled for a good balance for achieving a good preforming and a good **bottle** molding, same as in IV- .circle.6 .

DETDESC:

DETD(69)

IV- .circle.9 specifies the ratio of wall thicknesses of the inner **PES** layer and the outer **PES** layers. In other words, the ratio stands for a construction showing in which position in the tube wall the **EVOH** is located, and is, as explained in IV- .circle.5 and IV- .circle.7 a very important factor for tube molding technique and **bottle** molding technique, particularly **bottle** performance. In the case where **EVOH** layer is shifted outward, the tube and B/A is made smaller; when the tube is later processed into a gas barrier **container** for water-related beverages such as carbonated drinks, decrease in barrier property will be avoided to some extent. However since the inside gas pressure applied to the **EVOH** layer is also acted upon the thin outer **PES** layer, a delaminating stress in TR layer acting between the inner and outer layers of **PES** becomes large to

readily generate delamination between the **EVOH** layer and **TR** layer. On the other hand, in the case where **EVOH** layer is shifted inward and **B/A** is made larger, though it is preferred from viewpoint of delamination, **EVOH** layer is located closer to the contained liquid, i.e. to high-moisture area, to make the barrier property decrease. Accordingly it. . . be filled and the required performances such as pressure resistance, gas barrier property, etc. Generally speaking, for the gas barrier **containers** while it is unavoidable that the barrier property decrease due to moisture, the delamination problem can be solved by selecting bond strength of **TR**. Therefore it is recommended that the **EVOH** layer be shifted outward a little from the intermediate layer. Besides, when the wall thickness ratio **B/A** of the inner and outer **PES** layers is too high or too low, there readily forms a bias or nonuniformity in thickness of the thin **PES** layer, there becomes greater local nonuniformities in thickness of the **EVOH** layer which will cause streaks, and there readily generates a disorder (disorder in a thinner **PES** layer) of mouth at preform molding and that of bottom (e.g. bad junction due to disorder in a thinner **PES** layer), and so on. Accordingly the construction ratio is preferably $0.1 \leq B/A \leq 5$, more preferably $0.25 \leq B/A \leq 2.5$.

DETDESC:

DETD(70)

IV- . . . IV- .circle.13 are conditions of accuracy of wall thickness and thickness bias of **TR** layer. **TR** is a layer bonding **PES** layers with **EVOH** layer and has a particularly important meaning in preparing a biaxially drawn **container** from a multilayered tube. The **TR** layer must satisfy the following conditions:

DETDESC:

DETD(71)

(i) . . . of tube should be prevented by relaxing stress such as heat shrinkage caused by a difference in cooling degree between **PES** layers.

DETDESC:

DETD(73)

(iii) . . . preforms, nothing unusual such as unusual melting or bad fusion at the time of heating mouth and bottom of the **bottle**, may be allowed to happen.

DETDESC:

DETD(74)

(iv) At blow molding; a shear between **PES** layer and **EVOH** layer should be minimized so that the **EVOH** layer can be co-drawn uniformly with **PES** layer, and at the blow molding temperature, viscosity or Young's modulus should be kept high not to cause a delamination.

DETDESC:

DETD(75)

(v) No delamination should occur due to deformation of the **bottle** caused by internal pressure, by external force, etc.

DETDESC:

DETD(76)

(vi) The obtained **bottle** should satisfy other conditions in use (temperature, dropping, etc.)

DETDESC:

DETD(77)

For the purpose of obtaining a streakless **bottle**, the condition (iv), that is, TR being capable of allowing **EVOH** layer to be uniformly drawn is the most important. Therefore, an adhesive resin layer is not simply the one to be interposed between **PES** layer and **EVOH** layer, but is specified to satisfy the above conditions. Thus the thickness of the inner and outer layers, C and D are less than 10.mu., there tends to happen delamination from the **EVOH** layer caused by a difference in shrinkage stress on cooling in the tube molding process or by external stress on tube cutting, as well as by deformation stress due to internal gas pressure of the **bottle**.

DETDESC:

DETD(78)

On the other hand, in the case where the thickness exceeds 300.mu., in the course of blow molding, the bond between **PES** Layer and **EVOH** layer loosens, which lowers gripping effect to bring about a shear resulting in incapability of eliminating a nonuniformity in drawing the **EVOH** layer which is of poor drawability, so that streaks will readily be formed. Besides, a thickness more than required of. . .

DETDESC:

DETD(80)

Description will be made hereinbelow on a method of manufacturing the multilayered tube of this invention, which comprises **PES** layers as the inner and outer layers, an **EVOH** layer as an intermediate layer and TR layers interposed between the **PES** layers and the **EVOH** layer.

DETDESC:

DETD(82)

The present inventors have found it best to specify viscosities at 5.degree. C. above the melting point of **PES** resin having a melting point highest among **PES**, **EVOH** and TR, that is, to specify a viscosity index of any of polymers of **PES** resin, **EVOH** resin and TR resin at a temperature close to the melting point of **PES** (melting point of **PES** +5.degree. C.).

DETDESC:

DETD(83)

More . . . found that it is important to select a range of melt index (MI) value measured at the melting point of **PES** {MP(**PES**) } +5.degree. C. of each polymer (MFR determined by method A of JIS-K-7210 GENERAL TEST METHOD BY FLOWING WATER, load 2160. . .

DETDESC:

DETD(84)

0.3 g/10 min..ltoreq.MI(**PES**).ltoreq.10 g/10 min.

III-

.circle.1

DETDESC:

DETD(85)

1.0 g/10 min..ltoreq.MI(**EVOH**).ltoreq.25 g/10 min.

III-

.circle.2

DETDESC:

DETD(87)

0.2.ltoreq.MI(**EVOH**)/MI(**PES**).ltoreq.30

III-

.circle.4

DETDESC:

DETD(88)

0.5.ltoreq.MI(TR)/MI(**PES**).ltoreq.60

III-

.circle.5

DETDESC:

DETD(89)

0.2.ltoreq.MI(TR)/MI(**EVOH**).ltoreq.25

III-

.circle.6

DETDESC:

DETD(90)

PES is a principal resin constituting most part of a tube, and so it is not preferred, from viewpoint of practicality, to select taking into consideration only compatibility of viscosity factor with **EVOH** or TR, or that of temperature factor. Since tube formability and **bottle** moldability are of great importance for obtaining a good tube and a good **bottle** including quality items such as strength and transparency, the manufacturing conditions for **PES** tend to shift toward higher viscosities, higher melting points and lower modification degree, which are also influenced by productivity and . . . production cost, thus making it technically difficult to have a proper formation temperature and a proper viscosity match those of **EVOH** and TR. Further, because **EVOH** is a resin very sensitive to heat and being liable to gel or deteriorate by thermal decomposition, it is necessary to lower the temperature of **PES** to the lowest at which the molding is still possible. Generally it is preferred to carry out extrusion molding while decreasing the temperature close to MP(**PES**).

DETDESC:

DETD(91)

PES used preferably in this invention is the one which satisfies the condition III-.circle.1 . The prferred range is 0.7 g/10 min.ltoreq.MI(**PES**).ltoreq.10 g/10 min. [.eta.] of **PES** is 0.7 to 1.4, preferably 0.8 to 1.3. In the case where MI(**PES**) (at MP +5.degree. C.) exceeds 10 g/10 min, that is, when the melt viscosity is too low, on the occasion of coextrusion molding with **EVOH** tubular molten polymers having a multilayered construction extruded from a die will deform, in a passage starting at the exit. . . a thickness bias causing a difficulty in obtaining a uniform multilayered tube. On the other hand, in the case where MI(**PES**) is lower than 0.3 g/10 min., though the above-described deformation in the passage from the extrusion

to the cooling fixing. . . .

DETDESC:

DET D(92)

Viscosity of **EVOH** is also very important. For the purpose of preparing a clean layer having a minimum thickness bias and no minute thickness nonuniformities which will cause streaks in the **bottle**, it is specified that the proper range of viscosity coefficient be: MI(**EVOH**).ltoreq.25 g/10 min, more preferably MI(**EVOH**).ltoreq.20 g/10 min. In the case where MI is higher than 25 g/10 min; even in case the coefficient of melt viscosity of **PES** is in the above-described proper range, **EVOH** layer constituting an intermediate layer of the tube obtained by coextrusion molding of the two resins forms a number of streaky nonuniformities in thickness, so that a **container** prepared from the tube will have a very poor appearance and in utmost cases its properties such as the gas. . . .

DETDESC:

DET D(93)

On the other hand, a high polymerization-degree **EVOH** having a MI(**EVOH**) lower than 1.0 g/10 min has the following drawbacks:

DETDESC:

DET D(96)

difficult to coextrude with **PES**, and

DETDESC:

DET D(97)

requires special polymerization conditions for the production of the high polymerization degree **EVOH**, where there are limitations in equipment and production efficiency, thus not being industrially obtainable at a low cost.

DETDESC:

DET D(98)

Therefore MI(**EVOH**) is preferably 1.0 to 25 g/10 min, more preferably 2 to 20 g/10 min.

DETDESC:

DET D(99)

TR layer interposed between **PES** layer and **EVOH** layer has a function of adhering the **EVOH** layer to the **PES** layer and making effective co-drawing of **PES/EVOH** on blowing. The layer is preferably thinner, and the coefficient of viscosity can be selected from a wide range. Thus good molding is achieved when MI(TR) is 1.5 to 90 g/10 min at MP(**PES**)+5.degree. C. However if MI(TR) exceeds 90, the viscosity becomes very low to make difficult formation of the polymer flow as a uniform thin layer inside the die; and further in this case if the difference of viscosity between **PES** layer and **EVOH** layer is big, there readily occurs an unbalance of flow in the formation of multilayer laminar flow, generating pulsations or. . . . though the moldability of the resin itself becomes better and so there will be no problem unless the viscosity of **EVOH** is very low, the TR polymer having invaded into the flow pass of **EVOH** layer, which happens for instance at the time of starting the molding, will not easily be substituted with **EVOH** and tends to remain there to cause a disordered

flow of the **EVOH** layer. Therefore, MI(TR) is preferably 1.5 to 90 g/10 min, more preferably 2 to 75 g/10 min. As requirements for TR resin, while viscosity is important for a good multilayer flow of polymers, most important are adhesiveness with **PES** and **EVOH**, and co-drawability in blowing, as well as physicochemical properties including heat resistance, water resistance, appearance (transparency, etc.), and so on. . . .

DETDESC:

DETD(100)

III . . . - .circle.6 specify the applicable ranges of coefficient of viscosity of each resin. Concerning the ratio of viscosity coefficients of **EVOH/PES**, MI(**EVOH**)/MI(**PES**), though it is likely thought that because the two resins do not touch directly the ratio has no relationship with. . . . moldability, in practice it is not the case. Since TR layer is a very thin layer, and the flow of **PES** sensitively influences **EVOH** layer, the ratio MI(**EVOH**)/MI(**PES**) is important particularly when the ratio is high. In this case an irregularity in polymer flow of the high-viscosity side (**PES**) strongly affects flow of ;the low-viscosity flow (**EVOH**), destroys the balance of laminar flow, and readily makes form disorders such as irregularities of thickness or thickness bias caused. . . . and minute nonuniformities in thickness. Tendency to deform is more distinguished as the thickness becomes large. Thus the rather thick **PES** layer allows a selection of viscosity toward higher side, while the thinner TR layer can choose a viscosity of a. . . .

DETDESC:

DETD(101)

0.5.ltoreq.MI(**EVOH**)/MI(**PES**).ltoreq.20

DETDESC:

DETD(102)

0.5.ltoreq.MI(TR)/MI(**PES**).ltoreq.40

DETDESC:

DETD(103)

0.5.ltoreq.MI(TR)/MI(**EVOH**).ltoreq.25

DETDESC:

DETD(104)

Melt index (MI) used in this invention means a melt viscosity index of **PES**, **EVOH** or TR in a tube, and is defined as follows according to JIS-K-7210. ##EQU7## wherein: T: temperature measured {MP(**PES**)+5.degree. C.}

DETDESC:

DETD(108)

It is necessary that moisture contents of specimens for measuring melt viscosity index be reduced to 20 ppm or below for **PES**, 50 ppm or below for TR and 500 ppm or below for **EVOH** respectively by drying in vacuum or with hot air prior to the measurement.

DETDESC:

DETD(109)

PES used in this invention is representatively a **polyethylene** terephthalate-related polyester. As the polyester, there is a polyester resin being principally composed of a glycol component and an acid. . . . acid component. Examples of other glycol components are aliphatic glycols such as propylene glycol, trimethylene glycol, tetramethylene glycol, diethylene glycol, **polyethylene** glycol, polypropylene glycol, polytetramethylene glycol, hexamethylene glycol, dodecamethylene glycol and neopentyl glycol, alicyclic glycols such as cyclohexyl glycol and aromatic. . . . glycols may be contained in an amount not exceeding 20 mol% of the total glycol component. Composition of the inner **PES** layer and that of the outer **PES** layer may be the same or different from each other.

DETDESC:

DETD(110)

In this invention, in the case where the ethylene content of **EVOH** as the intermediate layer exceeds 55 mol%, the gas barrier property which is an excellent characteristic of the resin, becomes. . . . 20 mol% will make poor molding processability and can not be used in this invention. Accordingly the ethylene content of **EVOH** is preferably 20 to 55 mol%, more preferably 25 to 50 mol%. The saponification degree of vinyl acetate component is. . . . than 96 mol% decreases the gas barrier property and can not be put in practical use. In the preparation of **EVOH**, a monomer other than but copolymerizable with ethylene and vinyl acetate may be used for copolymerization followed by saponification, within. . . .

DETDESC:

DETD(111)

As TR which is interposed between the inner and outer **PES** layers and the intermediate **EVOH** layer according to this invention, preferred examples include ethylene-vinyl acetate copolymer grafted with an unsaturated carboxylic acid or anhydride thereof,

DETDESC:

DETD(112)

The invention may, as occasions demand, be further provided thereon another resin layers and the like; but it is preferred that **PES** layers be the utmost layers from viewpoint of mechanical strength and appearance. Further each layer of the multilayered tube may. . . .

DETDESC:

DETD(122)

Already explained are that the fundamentals of TR resin are adhesiveness in a multilayered tube and **bottle**, and compatibility of viscosity with those of other resins at the time of coextrusion molding, and drawability in blow molding coming next. Selection of TR has so far been made centering simply on adhesiveness. However for obtaining a good **bottle** having no streaks, it is also an indispensable matter for TR, while being incorporated between **PES** layer and **EVOH** layer, to harmonize with the moldabilities of both **PES** and **EVOH** which are largely different from each other, which is so one of the points for selection of TR.

DETDESC:

DETD(123)

TR is required to meet, while being incorporated between **PES** layer and **EVOH** layer in the passage inside the die, the following requirements:

DETDESC:

DETD(124)

.circle.1 capable of suppressing heat transfer from high-temperature **PES** to **EVOH** and thereby suppress overheating of **EVOH**, and

DETDESC:

DETD(125)

.circle.2 . . . preforming, by suppressing residual internal stress due to a difference of heat shrinkages at the sizing and cooling process between **PES** and **EVOH** and relaxing the residual internal stress.

DETDESC:

DETD(127)

(1) Melting point of TR should be much lower than the molding temperature of **PES**, and be as close to the melting point of **EVOH**. The preferred range is expressed as follows:

DETDESC:

DETD(128)

80.degree. C..ltoreq.MP(TR).ltoreq.MP(**EVOH**)+20.degree. C. III - .circle.7

DETDESC:

DETD(129)

MP(TR).ltoreq.MP(**PES**)-20.degree. C. III - .circle.8

DETDESC:

DETD(131)

(2) The resin should not, when contacted with a high temperature (molten **PES**), form deterioration or unusualness such as foaming and gelation and coloring, and should have a wide applicable range of molding.

DETDESC:

DETD(132)

(3) Melting point of TR should be higher than glass transition temperatures of **PES** and **EVOH**, and at the same time higher than the blow temperature of **bottle**, that is, should be 80.degree. C..ltoreq.MP(TR), more preferably 90.degree. C..ltoreq.MP(TR).

DETDESC:

DETD(133)

(4) The resin should be of lower elasticity than **PES** and **EVOH**.

While the elastic moduli of **PES** and **EVOH** are generally 12,000 to 32,000 kg/cm.sup.2, that of TR should be 6000 kg/cm.sup.2 or below, preferably:

DETDESC:

DETD(137)

SELECTION OF **EVOH** RESIN

DETDESC:

DETD(138)

EVOH is a resin having a great tendency to deteriorate by heat, and also having a technical difficulty in molding even. . . thereof only; and it has, regarding formation of the multilayered tube of this invention where the coextrusion with a high-temperature **PES** is necessary, still more difficulties so that the selection of the resin is very important. In selecting **EVOH**, while it has already been explained that the relationships of polymer viscosity at molding with **PES** and TR are the most important, considerations listed below are also important because of special characteristics of **EVOH**.

DETDESC:

DETD(139)

(1) **EVOH** is a resin of a very poor extrusion moldability, and has an annoying characteristic of readily forming heat deterioration and. . .

DETDESC:

DETD(140)

(2) **EVOH** is a resin having a particular tendency to deteriorate by heat. Therefore employment of a high precision filter which will. . .

DETDESC:

DETD(141)

(3) Though **PES** and other resins are used after drying to a low moisture content of about 50 ppm or below, such a high degree of drying of **EVOH** will cause a problem such as deterioration or degradation. Therefore moisture content of **EVOH** should be kept high, which will make better extrusion moldability, with a range not to cause deterioration by hydrolysis. The. . .

DETDESC:

DETD(142)

SELECTION OF **PES** RESIN

DETDESC:

DETD(143)

(1) For the selection of **PES**, the most important factors is fundamentally, as already explained, characteristics for molding tube represented by polymerization degree and viscosity.

DETDESC:

DETD(144)

(2) Though pure PET is most preferable from the viewpoints of economy and **bottle** properties, there is also often employed, considering factors of molding viscosities of **EVOH**, etc. and of whitening due to crystallization in a tube having a thicker wall, a polyester having shifted to a. . . for a thin wall tube having a wall thickness of 3 to 4 mm or below, pure PET or a **PES** closer thereto, modified slightly in an amount of 2 to 3 mol% is preferred; while for a thicker tube having a wall thickness of not less than 3.5 to 4 mm, a **PES** modified in an amount more than 2 to 3 mol%.

DETDESC:

DETD(146)

EXTRUSION CONDITIONS FOR **PES**

DETDESC:

DETD(147)

PES (particularly pure PET) of a high polymerization for tube molding tends to decrease its tube moldability if extrusion-kneading is insufficient. . . rotation. Thereupon due to self heating, the temperature raises to a considerably high temperature to make, if the high temperature **PES** in a large amount extruded is introduced as it is, the whole die be highly heated causing problems of **PES** itself such as viscosity decrease and generation of decomposed matters, as well as deterioration of TR and **EVOH** inside the die.

DETDESC:

DETD(148)

For . . . polymer pass 2-A, and so on. Here, too rapid cooling will cause a local supercooling to promote local crystallization of **PES** resulting in generation of a whitening problem. Further, when at 1-A of the extruder for **PES** there occur variations in amounts extruded, in temperature and in pressure, there will generate not only a variation in tube. . .

DETDESC:

DETD(149)

EXTRUSION CONDITIONS FOR **EVOH**

DETDESC:

DETD(150)

Since **EVOH** readily deteriorates by heat, which will cause, at places of stagnation or of a slow flow in the polymer pass, generation of abnormalities such as gels, foaming, coloring by degradation, etc., which will in turn mix into **EVOH** polymer to give streaks or "grains" (granular matters having mixed thereinto abnormal substances such as gels). Particularly, degraded matters having. . . at the pass confluence inside the die are the principal cause for generating streaks. For preventing the heat deterioration of **EVOH**, it comes at first to decrease the temperature of the polymer extruded. However, since **EVOH** having a high viscosity or high barrier property (having a low ethylene content) is used for multilayered tubes, a decrease. . .

DETDESC:

DETD(151)

Explained hereinbelow will be results of various studies performed by the present inventors for getting a good **EVOH** layer, with reference to an example of effective and important extrusion conditions.

DETDESC:

DET(153)

.circle.2 The rate of shear of **EVOH** at the metering zone of the extruder 1-B (consisting of a feed zone, compression zone and a metering zone) is. . . .

DETDESC:

DET(158)

As . . . extrusion of TR, that a polymer extrusion without forming irregular matters is important is same as in the case of **PES** and **EVOH**, for which it is required to select appropriate extrusion conditions meeting the TR to be used. Particularly important are setting. . . In the case where the TR temperature is too low as compared with that of the die temperature or of **PES**, the TR will flow incorporating a big nonuniformity of temperature, especially at the spiral mandrel, to cause nonuniform thicknesses and streaks. On the other hand, too high a TR temperature relative to the extrusion temperature of **EVOH** will heighten the **EVOH** temperature and decrease the effect of preventing **EVOH** from a high temperature **PES**, resulting in superheating of **EVOH**, which accelerates deterioration of the **EVOH** and increases the cause of streaks and nonuniform wall thickness. Therefore, the extrusion temperature of TR shall be selected, while. . . to some extent a deviation from the most appropriate molding temperature for TR itself, taking into consideration temperature balances with **EVOH** and **PES**. For example when **PES** having a melting point of 230.degree. to 255.degree. C., the standard temperature conditions are 255.degree. to 285.degree. C. for **PES** at the die entrance (265.degree. to 300.degree. C. at the highest temperature region of the extruder), 220.degree. to 260.degree. C. for **EVOH** at the die entrance, and 230.degree. to 260.degree. C. as the set temperature for the die mold. Thereupon, when the. . . .

DETDESC:

DET(159)

Next, . . . to a simple flow sheet. FIG. 5 is an example of a representative flow sheet of molding process for a **PES/TR/EVOH** 3 kind/5 layer tube manufacturing apparatus. 1-A, 1-B and 1-C are extruders each of which is provided with a feed zone, compression zone and a metering zone, for **PES**, **EVOH** and TR respectively. 2-A, 2-B and 2-C are passages of the three polymers, each of which is as occasions demand. . . . tube cutter which is a continuous tube cutter for cutting the running tube into short segments each corresponding to a **bottle** or into a little longer segments corresponding to a plurality of **bottles**.

DETDESC:

DET(161)

FIG. . . . 6-(2) is a sketch of the appearance of mandrel 23 constituting the die. 1 designates flow entrance of the inner **PES** layer, 2 that of the inner TR layer, 3 that of **EVOH**, 4 that of the outer TR and 5 that of the outer **PES**. 6 is the entrance of **PES**, 7 the branch point of **PES** flow, 8 the entrance of TR, 9 the branch point of TR and 10 the entrance of **EVOH**. **PES** supplied to the

entrance of the inner and outer **PES** layers 1 and 5 goes through spiral passages of mandrels 21 and 25 for the inner and the outer **PES** layers respectively, while being circumferentially uniformly distributed, to discharge slits 11 and 15 and finally to the confluence 16. Similarly, . . . 24 for **TR**, while being circumferentially uniformly distributed, to discharge slits 12 and 14 and finally to the confluence 16. **EVOH** goes in a similar manner starting at the entrance 3. At the confluence 16 the 3 kind/5 layer tubular multilayered. . . .

DETDESC:

DET^D(162)

FIG. 6(2) shows a sketch of the appearance of a mandrel for **EVOH**. **EVOH** polymer supplied to the entrance of the **EVOH** layer is circumferentially uniformly distributed by current evening function along a spiral groove 3', and introduced to the **EVOH** discharge slit 13. The entrance passage 3 consists of a plurality, which number depends on the diameter of the mandrel, . . . flows have almost no stagnation at passages of each mandrel (particularly in spiral passages) and distribute circumferentially uniformly. Particularly for **EVOH** passage, presence of not only stagnation region but also that of a region of slow flow are not preferred. Average flow rate for **EVOH** is preferably 0.2 cm/sec or higher. Also important is the smoothness of passages. For the **EVOH** passage, it is preferred to provide a plating with hard chrome, which is a metal having little tendency to deteriorate and having resin deposit to form when contacted closely with **EVOH**, having specular gloss with a surface roughness of 0.5 S or below, more preferably 0.1 S or below.

DETDESC:

DET^D(163)

The . . . as is restricted from machining precision and assembling precision. Generally the slit gauges are preferably 0.5 to 5 mm for **PES**, 0.2 to 1.2 mm for **EVOH** and 0.2 to 1.2 mm for **TR**, more preferably 0.8 to 3.0 mm for **PES**, 0.3 to 1.0 mm for **EVOH** and 0.3 to 1.0 mm for **TR**.

DETDESC:

DET^D(164)

The . . . is also very important, and so done fully to the gauge variation of less than about .+- .3%, and for the **EVOH** slit to a difference between maximum and minimum of less than about .+- .20. μ ., more preferably .+- .10. μ . or below. It is. . . slit shall be designated taking shear rate of the polymer as an important index, which is particularly important for the **EVOH** slit since the precipitation of deteriorated matters at the slit will greatly influence formation of streaks. Particularly preferred shear rate. . . .

DETDESC:

DET^D(166)

The . . . which is shown in FIG. 6-(2) is most appropriate, and that it is very important, particularly for a passage for **EVOH**, to make the mandrel structure have a smooth passage so that no stagnation will occur and as smooth a flow. . . . of streaks over a long period of time. The rate of shear at the exit of the discharge slit where **EVOH** layer meets **TR** layer and **PES** layer is made more than 30 sec.sup.-1, preferably more than 50 sec.sup.-1. This is necessary based on the following fact: . . . smooth passage which does not form stagnation, when the rate of shear is low, an increase in the viscosity of **EVOH** at a region of slow flow will occur due to thermal degradation of the

EVOH to make the flow rate slower to promote gelation, resulting in depositing of degraded matters on around the discharge slit, . . . nonuniformity of the polymer flow, to cause streaks to generate. Therefore, the rate of shear on the passage surface for **EVOH** must be made high to prevent formation of streaks. Further in the extrusion molding of **EVOH**, when a deformation of roughness caused by gelation once forms, it is almost impossible to resume the original good condition. . . .

DETDESC:

DETD(167)

Not . . . and having a one-by-one meeting system shown in FIG. 6. FIG. 7(2) is a die which first has TR and **PES** of the outer layers and inner layers meet and laminate with each other, and finally have the laminate meet **EVOH**. FIG. 7(3) is a die of simultaneous confluence system which has 5 layers meet at the same time. FIG. 7(4) is a die which first has **EVOH** and TR meet and thereafter has **PES** meet thereonto from the both sides. Die structures are fundamentally broken down from the standpoint of confluence system into the. . . .

DETDESC:

DETD(168)

Next, . . . operation at the start up of extrusion molding of tube, which is a very important technique for preparing a good **bottle** having no streaks, including also the properties and conditions of polymers and the die structure.

DETDESC:

DETD(169)

As . . . an increased discharging rate until molding becomes stable. In the coextrusion molding of the multilayered tube utilizing a high temperature **PES** and **EVOH** according to this invention, when **EVOH** invades into other passage or when **PES** of high temperature and high viscosity mixes into the **EVOH** passage, there will occur a viscosity increase and deterioration of stagnated **EVOH** because of its characteristics of readily deteriorating by heat, which causes **EVOH** to remain and deposit in the passage resulting in generation of streaks or gel-like grains. It is not expected that. . . . a roughness of the flow passage surface (minute deflection caused by deposit of degraded matters) is formed in the initial **EVOH** passage, such once worsened passage surface cannot be restored to the original state and it is very difficult to restore streaks of the **EVOH** layer to a better condition, even when improvement of the flow or cleaning of the passage surface is aimed at. . . .

DETDESC:

DETD(170)

Therefore, . . . i.e. the state of polymer being introduced into the inside of the die is very important, and particularly behavior of **EVOH** inside the die is the most important. As a result of a variety of studies made by the present inventors. . . . precisely controlled. As regards the order of introducing polymers, firstly TR is discharged to the confluence region to wet the **PES** slit, etc. at the confluence region, then introduce and discharge **EVOH** from the slit, followed by extruding **PES**. FIG. 13 is a diagrammatical drawing showing flows and a timing of discharge of the polymers at the die for. . . . the entrances 2 and 4 and discharged to the confluence region to wet each passage surface, and on this timing **EVOH** is introduced at a breath

from the entrance 3. Black area A designates TR. In FIG. 13(2) where **EVOH** has already been introduced, the flow passage surface is covered with TR to prevent an instantaneous sticking of **EVOH**. Hatched area of B shows **EVOH**. That is, **PES** is introduced to form FIG. 13(2). This type of starting method can prevent **EVOH** from sticking or invasion into other passages, and high-temperature **PES** from invading into the **EVOH** passage, making possible a good molding. In the case where the above method is not adopted and firstly **EVOH** is introduced, the **EVOH** invades into other passages and sticks thereto, and then stagnates and gels on the passage surface, which gels are difficult to substitute. Particularly, the **EVOH** having invaded into the TR passage will, since the viscosity of TR is not high and the shear stress of . . to deteriorate and gel further, depositing on the passage surface to cause streaks and grains. In the case when firstly **PES** is started, the **PES** invades into the **EVOH** passage. **PES** having adhered to the **EVOH** passage cannot, due to its high viscosity, be smoothly put out and substituted with **EVOH** discharged next, and forms a stagnation, as well as promotes thermal degradation of **EVOH** contacting the high temperature **PES**. Needless to say that when starting up it is necessary that the passage surfaces have been fully cleaned beforehand and that polymers (particularly **EVOH**) to be introduced be clean ones containing no foreign matters or unmolten matters.

DETDESC:

DETD(171)

Another . . . as those used for the molding, having low viscosities; whereas also effective is a method using other polymers such as **Polyethylene (PE)** and **Polypropylene (PP)**.

DETDESC:

DETD(173)

(i) (L) (2nd and 4th layers) **TR.fwdarw.**(L) (3rd layer)
EVOH.fwdarw.(L) (1st and 5th layers) **PES.fwdarw.**(N) (2nd and 4th layer) **TR.fwdarw.**(N) (1st and 5th layers) **PES.fwdarw.**(N) (3rd layer) **EVOH**

DETDESC:

DETD(174)

(ii) (2nd and 4th layers) **PE.fwdarw.**(L) (1st and 5th layers)
PE.fwdarw.(N) (3rd layer) **EVOH.fwdarw.**(N) (2nd and 4th layer)
TR.fwdarw.(N) (1st and 5th layers) **PES**

DETDESC:

DETD(175)

(iii) (L) (2nd and 4th layers) **TR.fwdarw.**(L) (3rd layer)
EVOH.fwdarw.(N) (1st and 5th layers) **PES.fwdarw.**(N) (2nd and 4th layer) **TR.fwdarw.**(N) (3rd layer) **EVOH**

DETDESC:

DETD(177)

Polystyrene, **nylon**, **high-modified PES**, and the like are also useful as polymers to be substituted. **EVOH** having a low viscosity used herein is selected from grades having a good thermal stability.

DETDESC:

DETD(178)

As still other methods for starting up, there are useful methods including a method which comprises adjusting extrusion rates of **PES**, **EVOH** and **TR** to obtain good flows, a method comprises cooling and substituting the inside of the die and the polymer passages (particularly **EVOH** passage) with an inert gas, and a method which comprises starting with polymers including **PES**, which can be extrudable at a low temperature of 200.degree. to 250.degree. C.

DETDESC:

DETD(179)

Next, explanations are made on multilayered **containers** obtained from the multilayered tubes of this invention.

DETDESC:

DETD(180)

There can be obtained a **bottle** having a good appearance substantially without streaks and being excellent in gas barrier properties, pressure proofness, shock resistance and transparency, . . . out biaxial blow molding thereof. Defects in appearance (streaks) which are seen linearly continuously in the longitudinal direction on the **bottle** body, are the ones observed as longitudinal streaky irregularities in appearance, each one of which is caused by nonuniform refraction of light through a resin lens formed by irregularity of thickness extending linearly in the longitudinal direction on the **bottle** body. This defect becomes a clearer streak as it grows big exceeding a certain size, which make the appearance nonuniform and feeling of nonequal quality, and the **bottle** loses the commercial value. The streaks of the **bottle** will further be elucidated below.

DETDESC:

DETD(181)

The **bottle** having substantially no streaks as used in this description means a **bottle**, excluding one having streaks originating from a shift of the matching planes of a mold or streaks added for decoration purpose, having utterly no longitudinally continuous region of optical nonuniformity on the **bottle** body caused by slight nonuniformities in thickness of the body wall, as well as ones of good appearance which do. . . irregular streaks of clearness of such degree as to spoil the appearance and to make a person who uses the **bottle** feel that the **bottle** is not good or has an unpleasant feeling.

DETDESC:

DETD(182)

As the result of a study on streaks on the **bottles** obtained by making preforms from tubes and biaxially blow molding them, it has been found that, among streaky nonuniformities on **EVOH** layer of the **bottle** body, such nonuniformity is clearly recognized as a streak that has a ratio of the difference between the maximum thickness (t_{max}) and the minimum thickness (t_{min}) in a segment in the **EVOH** layer between two points 100 to 500.mu. circumferentially apart from each other to the distance of the two points (L), that is, $(t_{max}-t_{min})/L$ is 1/1000 or higher. When a streak of this size is present on the **bottle**, the **bottle** will look bad and decrease its commercial value.

DETDESC:

DETD(183)

On the other hand a circumferential portion (**EVOH** layer) having the ratio of $(t_{max}-t_{min})/L$ of less than 1/1000 does not spoil the appearance quality of the **bottle** and does not decrease the commercial value of the **bottle**.

DETDESC:

DETD(184)

FIG. 1 shows a graph of thickness distribution circumferentially continuously measured on a specimen having an average thickness of 25. μ . of **EVOH** layer which specimen was taken from a circumference of the **bottle** body of a **PES/EVOH** multilayered **bottle**.

Measurement of thickness was done on the specimen of **EVOH** layer being moved at a constant rate, by using a continuous thickness tester having a curved surface probe R._{sub}3. Any . . . far as it can measure local thicknesses at the same level of precision. The ordinate represents the thickness of the **EVOH** layer in μ ., and the abscissa represents the circumferential distance of the **bottle** body in mm.

DETDESC:

DETD(185)

FIG. 1 shows that the thickness of the **EVOH** layer is not uniform and that there are nonuniformities in thickness.

DETDESC:

DETD(186)

Among . . . is marked on any point not less than 0.1 mm apart from A, and the difference of the thicknesses of **EVOH** layer at points A and B ($t_{max}-t_{min}$) and the distance between A and B (L) are measured, followed by calculation of the ratio $(t_{max}-t_{min})/L$. On a **bottle** having streaks which spoils the appearance and makes a person who uses the **bottle** feel that it is a bad **bottle** and has an unpleasant feeling, more than one part having the above ratio of 1/1000 are observed among the streaks.

DETDESC:

DETD(187)

On the other hand, on a **bottle** having substantially no streaks, that is, a **bottle** which does not have a streak of such clearliness as to give a bad impression and damage the commercial value of the **bottle**, there can not be found a portion having the above ratio of not less than 1/1000.

DETDESC:

DETD(188)

In . . . a bad streaky nonuniformity from a harmless streaky nonuniformity from the results of measurement of the thickness distribution of the **EVOH** layer of the **bottle**.

DETDESC:

DETD(189)

Preparation of a multilayered **container** from the multilayered tube of this invention is carried out as follows:

DETDESC:

DETD(190)

After . . . is mounted on a biaxial blow molding machine and is subjected to heat biaxial blow molding to give a multilayered **container** (**bottle**) having substantially no streaks and having a beautiful appearance.

DETDESC:

DETD(192)

It . . . than 1.5 times the preform length and that in the circumferential (radial) direction be not less than 2.5 times the **bottle** diameter. Particularly, in the case where the radial drawing ratio is small, the drawing of **EVOH** layer is insufficient and there tends to occur nonuniform drawing to make worse the **bottle** appearance as well as decrease mechanical strength. Further if the radial drawing ratio is made more than 3, since the drawability is increased because the **EVOH** layer is co-drawn with **PES** layers, unless there is no local irregularities of thickness or others, a uniform drawing can be performed to minimize generation. . .

DETDESC:

DETD(193)

Heating . . . a biaxial blow molding is done at a temperature 75.degree. to 130.degree. C., and it is preferred for obtaining a **bottle** of better appearance to heat at 80.degree. to 125.degree. C.

DETDESC:

DETD(194)

The thus obtained **bottle** has as described before substantially no streaks and is not only of a beautiful appearance but also excellent in gas barrier property, etc. and so preferably used for **bottles** for filling foods, beverages, alcohols, particularly carbonated drinks and beers, as well as medicines, cosmetics and the like.

DETDESC:

DETD(195)

In . . . cutting the enlarged tube to suitable lengths, and providing a stopper each at both ends thereof to give a can-shaped **container**.

DETDESC:

DETD(198)

A **polyethylene** terephthalate resin having MI at 255.degree. C. of $4\{\eta\} = 1.0$, MP determined by measurement with DSC (at a scanning speed of. . . layer tube, the temperatures of the die and the entrances thereof being 245.degree. C., and 280.degree. C. (PET), 250.degree. C. (**EVOH**) and 230.degree. C. (TR) respectively, to form a tube at a rate of 5 m/min to obtain a tube having. . .

DETDESC:

DETD(205)

Extrusion conditions for **EVOH**:

DETDESC:

DETD(210)

The average flow rate of **EVOH** in the die was 1.2 cm/sec or higher.

DETDESC:

DETD(211)

The rate of shear of **EVOH** in the die was 5 sec.sup.-1.

DETDESC:

DETD(212)

Both the polymer passages 2-A (PET) and 2-B (**EVOH**) were equipped with purging valves.

DETDESC:

DETD(213)

As . . . to a tolerance of 50.mu. or below for PET, 30.mu. or below for the adhesive resin, 20.mu. or below for **EVOH**. The average gauge of each slit was adjusted to 2 mm, 1 mm and 1 mm for PET, **EVOH** and the adhesive resin respectively. The adjustment was done by operating adjusting bolts for the mandrel position mounted on the. . .

DETDESC:

DETD(216)

A sketch of a cross section of the 3 kind/5 layer tube comprising PET as the inner and outer layers, **EVOH** as the intermediate layer and adhesive resin layers between the above two resin layers is shown in FIG. 8. The. . .

DETDESC:

DETD(217)

The 3 kind/5 layer tube was cut at 1-cm intervals, the **EVOH** layers were taken therefrom. After removing the adhesive resin sticking to the surface of the **EVOH** specimens by swelling with acetone, and drying, the **EVOH** layers were measured for minute thickness nonuniformities. The difference in thickness between any two points on the circumference each of. . .

DETDESC:

DETD(219)

The . . . machine made by the same company at a drawing ratio of 10 (axial drawing ratio.times.radial drawing ratio) to give a **bottle** having a capacity of 0.5 l, a height of 17.5 cm and an outer diameter of 72 mm.phi..

DETDESC:

DETD(220)

The thus obtained **bottle** was, as shown in FIG. 9, of a good appearance having substantially no streaks. The average thickness construction of the layers of the **bottle** body is shown in Table 5. The lateral thickness distribution of the **EVOH** layer taken out from

the **bottle** body was as shown in FIG. 11 and shows no thickness irregularity compared to Comparative Example 1 (FIG. 12) and no streaks at all which would worsen the **bottle** appearance. The thickness distribution was measured using a **continuous film thickness** tester made by ANRITSU ELECTRIC.

DETDESC:

DETD(223)

The . . . were adjusted to tolerances of not more than 40.mu., not more than 20.mu. and not more than 20.mu. for PET, **EVOH** and the adhesive resin respectively by operating adjusting bolts for the mandrel position mounted on the die. The average gauge of each slit was adjusted to 2 mm, 1 mm and 1 mm for PET, **EVOH** and the adhesive resin respectively. During the operation a change in operating conditions was done gradually in order that the pressure inside the die would not change abruptly. The extrusion conditions for PET, **EVOH** and TR were same as in Example 1 except for the extrusion temperature. The polymer passages 2-A, 2-B and 2-C. . . was attained. After the extrusion of each resin became steady, the purging valves were switched over successively to introduce TR, **EVOH** and PET in sequence at an appropriate timing into the die.

DETDESC:

DETD(225)

The **EVOH** layers in the specimens cut at 1-cm intervals from the tubes were checked for thickness nonuniformity in the same manner. . .

DETDESC:

DETD(226)

The . . . into a preform using the laboratory machine described in Example 1, and the preform was then molded into a blow **bottle** at a drawing ratio of 10 and at 95.degree. C. The obtained **bottle** had a capacity of 0.5 l, a height of 17.5 cm and an outer diameter of 72 mm, and showed substantially no streaks which would spoil the appearance of the **bottle**. Though compositions of PET and **EVOH** resins were different from those of Example 1, a proper selection of resin viscosities and attentions paid to consolidating the die and changing the operating conditions could lead to a preparation of a tube suitable for molding a **bottle** having an excellent appearance.

DETDESC:

DETD(228)

One of **PES** resins of the same kind as in Example 2 having MI's given in Table 1 and Table 2, **EVOH** (MP: 179.degree. C.) having an ethylene content of 33 mol% and a saponification degree of 99.5 mol% and an adhesive. . .

DETDESC:

DETD(229)

Assembling and operation were done in a similar manner to those in Example 2. Extrusion conditions for PET, **EVOH** and TR were nearly the same as in Example 1 except for the temperatures. The result of the moldings are summarized in Tables 1 and 2. The thickness nonuniformity between any two points on the circumference of an **EVOH** layer (cross section cut at 1-cm intervals) 100.mu. to 500.mu. distant from each other satisfied the condition II.

DETDESC:

DET(230)

The obtained tubes were molded using the blow molding machine described in Example 1 (drawing ratio: 10, at 105.degree. C.) into **bottles** having a capacity of 0.5 l, a height of 17.5 cm and a diameter of 72 mm.

DETDESC:

DET(231)

The thus obtained **bottles** showed substantially no streaks which would spoil the appearance.

DETDESC:

DET(232)

The constructions of the tubes and **bottles** obtained in Examples 1 to 9 are shown in Tables 1 and 2.

DETDESC:

DET(235)

Each . . . kind/5 layer die, and when the extrusion state became stable, introduced into the die in the order of PET, high-viscosity **EVOH** and TR by switching over the valves. As to the timing of the introduction, after confirming the discharge of a . . .

DETDESC:

DET(236)

Extrusion . . . same manner as in Example 1, except that the extrusion temperature for PET was 295.degree. C., the extrusion temperature for **EVOH** was 295.degree. C. and the rate of shear of **EVOH** in the metalling zone of the extruder and that in the die were 18 sec.sup.-1 and 21 sec.sup.-1 respectively, and. . .

DETDESC:

DET(237)

The **EVOH** layer taken out from the obtained tube showed a number of streaky thickness nonuniformities in a direction parallel to the tube axis. In the **EVOH** layer (cross section cut at 1-cm intervals), there were observed not less than 13 spots in a cross section, and. . .

DETDESC:

DET(238)

The . . . with a machine described in Example 1 into preforms, which were then subjected to a biaxial blow molding to give **bottles** having a capacity of 0.5 l. On all of the thus obtained **bottles**, there were observed: clearly distinguishable streaks(S): ca 8 in average/**bottle** slightly distinguishable streaks: many and the **bottle** appearances were spoiled (FIG. 10). A **bottle** was selected at random from these **bottles** and then the **EVOH** layer was taken out, followed by measurement for thickness distribution using the before-described continuous thickness tester. The result is shown. . . 12. About 8 spots were found to have big differences in thickness and they were thought to be causing the **bottle** to show the clear streaks.

DETDESC:

DETD(239)

It was not successful to reduce these streaks and to improve the appearance of the **bottle**, though various adjustments had been conducted on blow molding conditions to find a most suitable condition. Conversely, some adjustments resulted in an increase of streaks. From the above it can be understood that for getting **bottles** having no streaks it is important to prepare tubes having no streaks and also to have molding technique of a. . .

DETDESC:

DETD(241)

A **PES** having an [.eta.] different from that in Example 1, a saponified product of ethylene-vinyl acetate copolymer (**EVOH**) having an ethylene content of 32 mol% and a saponification degree of 99.5 mol%, and an adhesive resin of similar kind to that in Example 2 were in combination molded into 3 kind/5 layer tubes having the **EVOH** as the intermediate layer in the same manner as in Example 1, wherein however, at least one of the three. . . The MI's of resins used in each one of the Comparative Examples were as shown in Table 3: MI of **EVOH** in Comparative Example 2, MI's of **EVOH** and PET in Comparative Example 3, MI's of **EVOH**, PET and TR in Comparative Example 4, MI or TR in Comparative Example 5 and MI's of PET in Comparative Example 6 were not in the preferred range respectively. Each **EVOH** layer was taken out from each one of the obtained tubes, and the cross sections thereof cut at 1-cm intervals. . .

DETDESC:

DETD(242)

These tubes were molded into preforms using a machine described in Example 1, followed by biaxial blow molding thereof to give **bottles** having a capacity of 0.5 l. On each **bottle**, there were observed not less than 4 clear streaks and a number of slightly distinguishable small streaks. The appearances of the **bottles** were as bad as those in Comparative Example 1 which is illustrated in FIG. 10. Any change in blow molding conditions could not lead to obtaining a **bottle** having a good appearance and having substantially no streaks.

DETDESC:

DETD(243)

From the above it can be understood that for getting **bottles** having no streaks it is important to prepare tubes having no streaks, and that for getting a tube having no. . .

DETDESC:

DETD(244)

The constructions of the tubes and **bottles** obtained in Comparative Examples 1 to 6 are shown in Tables 3 and 4.

DETDESC:

DETD(245)

TABLE 1

Example 1 Example 2 Example 3 Example 4 Example

5

EVOH Layer (3rd Layer)

Average thickness (.mu.) .sup.--E

340 280 310 290 300

Max. thickness E (E/.sup.--E)

400(1.18) 305(1.09) 345(1.11) . . . 24.8 24.9

24.8

Hmax/.sup.--H

1.01 1.01 1.01 1.01 1.00

Hmin/.sup.--H

0.99 0.99 0.99 0.99 0.99

Ratio of MI's

MI(EVOH)/MI(PET)

1.5 5.3 2.0 6.7 0.8

MI(TR)/MI(PET)

6.3 20 20 20 3.8

MI(TR)/MI(EVOH)

4.2 3.8 10 3.0 5.0

Bottle

Appearance of **bottle**

good good good good good

Average thickness of

34 29 30 30 29

EVOH layer

DETDESC:

DETD(246)

TABLE 2

Example 6 Example 7 Example 8 Example 9

EVOH Layer (3rd Layer)

Average thickness (.mu.) E

300 300 310 300

Max. thickness E (E/.sup.--E)

350(1.17) 365(1.22) 360(1.16) . . . Hmin 24.8 24.8

24.8 24.7

Hmax/.sup.--H

1.01 1.008 1.01 1.01

Hmin/.sup.--H

0.99 0.992 0.99 0.99

Ratio of MI's

MI(EVOH)/MI(PET)

2.5 3.8 1.4 1.4

MI(TR)/MI(PET)

3.8 3.8 4.3 7.1

MI(TR)/MI(EVOH)

1.5 1.0 3.0 5.0

Bottle

Appearance of **bottle**

good good good good

Average thickness of

29 29.5 30.5 30

EVOH layer

DETDESC:

DETD(247)

TABLE 3

Comparative		
Comparative		
Comparative		
Example 1	Example 2	Example 3
EVOH Layer (3rd Layer)		
Average thickness (.mu.)	.sup.--E	
350	250	300
Max. thickness E (E/.sup.--E)		
430(1.23)	300(1.20)	365(1.22)
Min.. . .	25.3	25.4
Minimum Hmin	24.7	24.7
Hmax/.sup.--H		
1.01	1.01	1.02
Hmin/.sup.--H		
0.99	0.99	0.99
Ratio of MI's		
MI (EVOH)/MI (PET)		
1.5	7.5	2.0
MI (TR) /MI (PET)		
6.3	7.5	2.0
MI (TR) /MI (EVOH)		
4.2	1.0	1.0
Bottle		
Appearance of bottle		
streaks	streaks	streaks
Average thickness of		
34	24	29
EVOH layer		

DETDESC:

DETD(248)

TABLE 4

Comparative		
Comparative		
Comparative		
Example 4	Example 5	Example 6
EVOH Layer (3rd Layer)		
Average thickness (.mu.)	.sup.--E	
300	300	300
Max. thickness E (E/.sup.--E)		
375(1.25)	380(1.27)	360(1.20)
Min.. . .	25.3	25.5
Minimum Hmin	24.5	24.7
Hmax/.sup.--H		
1.02	1.01	1.02
Hmin/.sup.--H		
0.98	0.99	0.98
Ratio of MI's		

MI (EVOH) / MI (PET)	2.0	0.86	0.4
MI (TR) / MI (PET)	6.3	15.0	2.0
MI (TR) / MI (EVOH)	3.2	17.5	5.0

Bottle

Appearance of bottle	streaks	streaks	streaks
Average thickness of			
29	30	30	
EVOH layer			

DETDESC:

DETD (249)

TABLE 5

	Comparative		Comparative		Comparative		Comparative	
Example 1								
Example 2								
Example 3								
Example 4. . . layer								
(adhesive resin layer)								
(.mu.)								
Average thickness of	34	29	30	30	29	34	24	29
the 3th layer								
(EVOH) (.mu.)								
Average thickness of	8	7	7	7	8	8	5	7
the 2th layer								
(adhesive resin layer)								
(.mu.). . . thickness of	190	230	140	150	180	180	190	200
the 1th layer								
(inner PET layer) (.mu.)								
Appearance of bottle	good	good	good	good	good	no good		
						no good		
(streaks) no streaks							no good	
no streaks. . .								

CLAIMS:

CLMS (2)

2. . . . draw molding according to claim 1, wherein the following conditions III- .circle.1 to III- .circle.6 are satisfied:

0.3 g/10 min.ltoreq.MI (PES).ltoreq.10 g/10 min III-
.circle.1

1.0 g/10 min.ltoreq.MI (EVOH).ltoreq.25 g/10 min III-
.circle.2

1.5 g/10 min.ltoreq.MI (TR).ltoreq.90 g/10 min III-
.circle.3

0.2.ltoreq.MI(**EVOH**)/MI(**PES**).ltoreq.30
.circle.4

III-

0.5.ltoreq.MI(TR)/MI(**PES**).ltoreq.60
.circle.5

III-

0.2.ltoreq.MI(TR)/MI(**EVOH**).ltoreq.25
.circle.6

III-

80.degree. C..ltoreq.MP(TR).ltoreq.MP(**EVOH**)+20.degree. C. III-
.circle.7

MP(TR).ltoreq.MP(**PES**)-20.degree. C. III-
.circle.8

200 kg/cm.sup.2 .ltoreq.E(TR).ltoreq.6000 kg/cm.sup.2 III- .circle.
9

wherein:

MI: Melt flow index (g/10 min) measured at a temperature 5.degree. C.
higher than the melting point of the saturated polyester,

PES: saturated polyester,

EVOH: a saponified product of ethylene-vinyl acetate copolymer

TR: adhesive resin

MP: melting point

E: Young's modulus.

CLAIMS:

CLMS (3)

3. A method of producing a multilayered **container**, which comprises preparing a preform from a multilayered tube used for blow molding, which comprises a saturated polyester as the. . . .
:3 ab

US PAT NO: 4,534,930 [IMAGE AVAILABLE]

L6: 3 of 27

ABSTRACT:

A process for producing a stretched multilayer polyester **bottle** which comprises axially stretching a bottomed multilayer preform comprised of an inside and an outside polyester surface layer and an interlayer of a gas-barrier resin provided therebetween optionally through an adhesive under conditions which induce molecular orientation of the polyester and simultaneously stretching it circumferentially by blowing. The multilayer preform is produced by coating a solution or emulsion of an **ethylene-vinyl alcohol** copolymer on one surface of a primary preform of the polyester molded in advance, drying the coated preform at a temperature at which no whitening owing to the crystallization of the polyester occurs to thereby form a thin but **continuous film** of the **ethylene-vinyl alcohol** polymer on the primary preform, mounting the coated pre-form on an injection mold, and injection the polyester onto the coated layer to form the inside or outside surface layer of the polyester. This process enables the **ethylene-vinyl alcohol** copolymer to be interposed as the interlayer of the stretched polyester **bottle** in a thickness which does not hamper the stretching operation but is sufficient to ensure its gas-barrier property.
:d kwic

US PAT NO: 4,534,930 [IMAGE AVAILABLE]

L6: 3 of 27

TITLE: Process for producing stretched multilayer polyester
bottle

ABSTRACT:

A process for producing a stretched multilayer polyester **bottle** which

comprises axially stretching a bottomed multilayer preform comprised of an inside and an outside polyester surface layer and an . . . and simultaneously stretching it circumferentially by blowing. The multilayer preform is produced by coating a solution or emulsion of an **ethylene-vinyl alcohol** copolymer on one surface of a primary preform of the polyester molded in advance, drying the coated preform at a temperature at which no whitening owing to the crystallization of the polyester occurs to thereby form a thin but **continuous film** of the **ethylene-vinyl alcohol** polymer on the primary preform, mounting the coated pre-form on an injection mold, and injection the polyester onto the coated layer to form the inside or outside surface layer of the polyester. This process enables the **ethylene-vinyl alcohol** copolymer to be interposed as the interlayer of the stretched polyester **bottle** in a thickness which does not hamper the stretching operation but is sufficient to ensure its gas-barrier property.

SUMMARY:

BSUM(3)

This invention relates to a process for producing a stretched multilayer polyester **bottle**, and more specifically, to a process for producing a stretched multilayer polyester **bottle** the characteristic, of which lies in the production of a multilayer polyester preform.

SUMMARY:

BSUM(5)

It is known that biaxial stretching of a thermoplastic polyester capable of being oriented by stretching, such as **polyethylene** terephthalate, improves its appearance such as transparency, its mechanical properties such as rigidity and its dimensional stability. Biaxial stretching has long been utilized for molding of **containers**. A **container** having a biaxially oriented wall is produced by extrusion-molding or injection-molding the aforesaid thermoplastic polyester into a bottomless or bottomed. . . .

SUMMARY:

BSUM(6)

The biaxially stretched **container** has excellent transparency, rigidity, impact strength and dimensional stability, but does not prove satisfactory in its gas-barrier property. For example, a biaxially stretchable polyester such as **polyethylene** terephthalate, even after stretching, has a far higher oxygen permeability than a resin having high gas-barrier property such as a

SUMMARY:

BSUM(7)

It has already been known that to improve the gas-barrier property, particularly the oxygen-barrier property, of a biaxially stretched **container**, the orientable thermoplastic polyester is used in combination with an oxygen-barrier resin to provide a biaxially stretched multilayer **container**. For example, U.S. Pat. No. 3,733,309 discloses that in the production of a stretched blow-molded **container** from a preform of a polyester, an improvement in its gas-barrier property is expected by making the preform in a multilayer structure composed of the polyester and an **ethylene-vinyl alcohol** copolymer. The U.S. Patent, however, gives no specific disclosure about how this multilayer preform is produced.

SUMMARY:

BSUM(8)

For . . . (see, for example, Japanese Laid-Open Patent Publication No. 111,236/1980). The production of a multilayer preform of the aforesaid polyester and **ethylene-vinyl alcohol** copolymer by this multi-stage injection molded method gives rise to a problem in that the thickness of the **ethylene-vinyl alcohol** copolymer layer is difficult to adjust to not more than 1.0 mm in view of the balance between the melting--flowing and the cooling--solidification of the copolymer. The **ethylene-vinyl alcohol** copolymer with a thickness above 1.0 mm is very difficult to stretch under the polyester stretching conditions and economically, too, it is desired to reduce the thickness of the **ethylene-vinyl alcohol** copolymer layer.

SUMMARY:

BSUM(9)

Japanese . . . of an orientable thermoplastic resin such as a polyester with a solution or emulsion of a resin other than the **ethylene-vinyl alcohol** copolymer, for example a resin, such as a vinylidene chloride copolymer, which is impossible or difficult to heat-mold and has. . . .

SUMMARY: .

BSUM(10)

The present inventor has found that these problems can all be solved by coating a solution or emulsion of an **ethylene-vinyl alcohol** copolymer on a primary preform of a polyester, drying the preform at a temperature at which no whitening of the. . . .

SUMMARY:

BSUM(12)

It is an object of this invention to provide a process for producing a stretched multilayer polyester **bottle**, in which a gas-barrier layer composed of an **ethylene-vinyl alcohol** copolymer can be interposed as an interlayer of the stretched polyester **bottle** in a uniform thickness which does not hamper the stretching operation but is sufficient to ensure its gas-barrier property.

SUMMARY:

BSUM(13)

Another . . . of this invention is to provide a process for producing a multilayer bottom preform for the production of a stretched **bottle**, in which the bottomed preform for stretch blowing is formed by the injection of a polyester in two stages with a step of coating a solution or emulsion of an **ethylene-vinyl alcohol** copolymer interposed therebetween; whitening of the polyester owing to its crystallization is prevented in the coating step; and in the. . . .

SUMMARY:

BSUM(14)

Still another object of this invention is to provide a process for producing a stretched multilayer **bottle** which has excellent operability in stretching and can form an interlayer of an **ethylene-vinyl alcohol** copolymer having a relatively uniform thickness and being free from imperfections such as cracks.

SUMMARY:

BSUM(15)

According to this invention, there is provided a process for producing a stretched multilayer polyester **bottle** which comprises axially stretching a bottomed multilayer preform comprised of an inside and an outside polyester surface layer and an . . . simultaneously stretching it circumferentially by blowing; wherein said multilayer preform is produced by coating a solution or emulsion of an **ethylene-vinyl alcohol** copolymer on one surface of a primary preform of the polyester molded in advance, drying the coated preform at a temperature at which no whitening owing to the crystallization of the polyester occurs to thereby form a thin but **continuous film** of the **ethylene-vinyl alcohol** polymer on the primary preform, mounting the coated preform on an injection mold, and injecting the polyester onto the coated. . . .

SUMMARY:

BSUM(16)

According to the above process, the film of the **ethylene-vinyl alcohol** copolymer on the primary preform is formed in such a distribution that it is thick at the bottom of the. . . .

DRAWING DESC:

DRWD(2)

FIG. 1-A is a side sectional view of a biaxially stretched multilayer molded **bottle** produced by the present invention;

DRAWING DESC:

DRWD(3)

FIG. 1-B is an enlarged sectional view of the wall of the **bottle** shown in FIG. 1-A;

DRAWING DESC:

DRWD(13)

FIG. 8 is an enlarged sectional view of the vicinity of the neck portion of the **bottle** shown in FIG. 1.

DETDESC:

DETD(3)

In FIG. 1 which shows a biaxially stretched multilayer molded **bottle** in accordance with this invention, the **bottle** 1 consists of a mouth portion 2 equipped with a mechanism (such as a screw or bead) for clamping a. . . .

DETDESC:

DETD(4)

As is clear from the sectional portion of FIG. 1, the wall of the **bottle** includes an inside surface layer 5 and an outside surface layer 6 each formed of a thermoplastic polyester resin, and between the surface layers 5 and 6 is interposed a gas bar barrier layer 7 composed of an **ethylene-vinyl alcohol** copolymer applied as a solution

or emulsion. As required, adhesive resin layers 8 and 9 are provided between the gas-barrier. . . .

DETDESC:

DETD(5)

In the present invention, an **ethylene-vinyl alcohol** copolymer is selected as the gas-barrier resin because of its excellent gas-barrier property, and among various molecularly orientable resins, thermoplastic polyesters such as **polyethylene terephthalate** are selected because of their marked improvement in impact strength, rigidity, transparency, etc. by molecular orientation. Furthermore, a laminated. . . outside surface layer of the polyester and an interlayer of the copolymer is employed because the gas-barrier property of the **ethylene-vinyl alcohol** copolymer is greatly reduced by humidity.

DETDESC:

DETD(6)

It is important in the present invention that a bottomed multilayer preform is used in the production of the stretched multilayer **bottle**. By using the bottomed preform in stretching blow molding, it can be simultaneously stretched axially by a stretching bar and circumferentially by blowing. When the **ethylene-vinyl alcohol** copolymer is stretched successively in two directions, cracks are seen to form in the second stretching running in a direction. . . .

DETDESC:

DETD(7)

The process steps for producing the **bottle** in accordance with this invention is described below with reference to FIGS. 2-A to 7.

DETDESC:

DETD(9)

Then, . . . step. The preform 11 is dipped in the coating pot 13 to coat a solution or latex 14 of an **ethylene-vinyl alcohol** copolymer on its surface. Prior to the coating of the solution or latex 14, an adhesive or an anchoring agent. . . .

DETDESC:

DETD(10)

The **ethylene-vinyl alcohol** copolymer advantageously has a vinyl alcohol unit content of 50 to 95 mole%, particularly 55 to 85 mole%, in view. . . that since the copolymer is applied not by heat molding but in the form of a solution or emulsion, an **ethylene-vinyl alcohol** copolymer having a high vinyl alcohol unit content can also be used. Naturally, this copolymer should have a molecular weight. . . .

DETDESC:

DETD(11)

Any desired solvents known per se are used for the **ethylene-vinyl alcohol** copolymer. For example, there may be used dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, isopropanol, water, or combinations of at least two of. . . solvent. The solution is used for

coating, if required while maintaining it at a high temperature below 100.degree. C. The **ethylene-vinyl alcohol** copolymer can also be used in the form of an emulsion or latex suspended in an aqueous medium by an. . . .

DETDESC:

DETD(13)

In . . . invention, the wet film formed is dried at a temperature at which no whitening owing to the crystallization of the **polyethylene** occurs. As a result, a thin but **continuous film** of the copolymer is formed on the primary preform.

DETDESC:

DETD(14)

The . . . preform is prevented. Consequently, the excellent operability of the preform in stretching is maintained, and the transparency of the final **bottle** is increased.

DETDESC:

DETD(15)

Secondly, coupled with the coating of the **ethylene-vinyl alcohol** copolymer in the form of a solution or emulsion, the drying treatment under the above conditions can give a gas-barrier layer having a uniform thickness sufficient to ensure its gas-barrier property at every part of the final **bottle**. When the drying is carried out at a temperature at which whitening owing to the crystallization of the polyester is. . . . On the other hand, as already pointed out above, when the polyester is injected onto the coated layer of the **ethylene-vinyl alcohol** copolymer, the coated layer at the bottom portion is pushed toward the downstream side by the injecting pressure and becomes. . . .

DETDESC:

DETD(16)

It . . . that with regard to this feature of the present invention, satisfactory results are obtained if the coated film of the **ethylene-vinyl alcohol** copolymer is formed such that its thickness at the bottom portion of the preform becomes 3 to 15 times, especially. . . . the coated film may be 5 to 100 microns in the final preform, and 1 to 20 microns in the **bottle**.

DETDESC:

DETD(19)

The . . . as the adhesive resin which may, if desired, be applied to the primary preform prior to the coating of the **ethylene-vinyl alcohol** copolymer, or may be applied further after the coating of the copolymer.

DETDESC:

DETD(26)

The . . . end 15c of the side wall portion. In this specific embodiment, the neck portion 15c has no coating of the **ethylene-vinyl alcohol** copolymer formed thereon because the polyester remains there in a large thickness.

DETDESC:

DETD(36)

In the present invention in which the **bottle** is comprised of an inside and an outside PET layer and a coated interlayer of the **ethylene-vinyl alcohol** copolymer, each of these layers can be controlled to a prescribed thickness while avoiding a short mold by providing such. . . .

DETDESC:

DETD(37)

Polyethylene terephthalate, polybutylene terephthalate, etc. having film-forming molecular weights are conveniently used as the thermoplastic polyester constituting the inside and outside. . . .

DETDESC:

DETD(38)

Polyethylene terephthalate also includes crystalline copolymers containing in the polymer chain a small amount of comonomer units, for example diols other. . . .

DETDESC:

DETD(39)

The 5 and 6 is respectively 1.1 to 5.0 mm in the preform, and 100 to 500 microns in the blow-molded **bottle**. . . .

DETDESC:

DETD(40)

The blown from the stretching bar 21 to stretch and blow-mold the preform 18. As a result, the biaxially stretched multilayer **bottle** 1 is formed.

DETDESC:

DETD(43)

According to this invention, there is also provided a packing plastic **bottle** produced by the biaxially stretching blow-molding of a multilayer preform composed of an inside and an outside surface layer of a thermoplastic polyester and a gas barrier interlayer comprising an **ethylene-vinyl alcohol** copolymer and provided therebetween optionally through an adhesive layer and having a neck portion to be engaged with a closure, . . . of the bottom portion, body portion and shoulder portion being integrally molded from a thermoplastic polyester, said interlayer of the **ethylene-vinyl alcohol** copolymer being in the form of a continuous and seamless film extending over the bottom portion, body portion and shoulder portion with its upper end terminating immediately below the neck portion, said **ethylene-vinyl alcohol** copolymer layer having a thickness of 1 to 20 microns, and the neck portion and the thermoplastic polyester outside wall. . . .

DETDESC:

DETD(44)

In FIG. 8 which shows on an enlarged scale the principal parts of this

bottle, i.e. this vicinity of the neck portion, in section, the neck portion 2 has formed therein an open end 22, . . .

DETDESC:

DETD(45)

Since the primary preform is coated with a solution or emulsion of the **ethylene-vinyl alcohol** copolymer and dried to form a film, followed by stretching blow-molding, the interlayer 7 of this copolymer exists as a . . . and has a thickness in the range of 1 to 20 microns, especially 3 to 10 microns in the final **bottle**. The formation of such a thin, completely continuous interlayer has become possible for the first time by the present invention. . . . biaxial stretching blow-molding from a co-extrusion pipe cannot avoid the formation of a seam at the bottom of the resulting **bottle**, and this portion becomes defective in regard to gas barrier property. On the other hand, by an ordinary multilayer injection-molding. . . .

DETDESC:

DETD(47)

By . . . adjust the thickness of the interlayer resin layer to a desired value required for the gas barrier property of the **bottle** from the viewpoint of operability in stretching. Consequently, the amount of the expensive gas-barrier resin can be reduced, and the cost of the preform, and therefore the **bottle**, can be curtailed.

DETDESC:

DETD(48)

As . . . suitable for the blow stretching of the polyester. On the other hand, in many cases, oxygen-barrier resins such as the **ethylene-vinyl alcohol** copolymer are difficult to stretch under these conditions. Since in the present invention the gas-barrier resin is sandwiched by the. . . .

DETDESC:

DETD(50)

When . . . its end is necessarily exposed to the mouth portion of the preform, and therefore the mouth portion of the final **bottle**, and is directly affected by water in the **bottle** or the humidity of the inside of the **bottle** (the humidity of the inside of the **bottle** is considered to be 100% as a relative humidity) (the gas-barrier property of the **ethylene-vinyl alcohol** copolymer is markedly reduced under high humidity conditions). In contrast, according to the present invention, the exposing of this end portion to the mouth portion of the closed **bottle** can be prevented even if the gas-barrier resin layer exists also on the seam. This is because the neck portion. . . .

DETDESC:

DETD(51)

The . . . stretching, there is no tendency toward the occurrence of chipping, scratching, etc. at the seam portion, and a stretched blow-molded **bottle** having an especially good appearance can be obtained.

DETDESC:

DETD(54)

A primary bottomed preform of **polyethylene** terephthalate (inherent viscosity 0.82) having a length of 120 mm, an inside diameter of 25 mm and a side wall. . . with hot air at 90.degree. C. for 2 minutes. The coated preform was then dipped in a solution of an **ethylene-vinyl alcohol** copolymer having a vinyl alcohol content of 82 mole % in a mixture of propanol and water and then dried. . .

DETDESC:

DETD(55)

The . . . adjusted to one at which it had elastic deformability. Then, the preform was inserted into an injection mold (core) and **polyethylene** terephthalate having an inherent viscosity of 0.82 was injected onto the coated surface (outside surface) of the coated preform to. . . preform was thick (about 22 microns) at its side portion which would be stretched at a high stretch ratio in **bottle** molding, and thin at the vicinity of its upper end and at its bottom portion at which the stretch ratio. . .

DETDESC:

DETD(56)

The . . . preform was conditioned to a temperature of 95.degree. C., and then biaxially stretched and blow-molded to give a stretched multilayer **bottle** having an average body thickness of about 250 microns and an inner capacity of 500 cc. The thickness of the coated film of the **bottle** was uniform.

DETDESC:

DETD(57)

The **bottle** had an oxygen permeability of 2.4 cc/m.².day.atm. (37.degree. C.) which was less than one-fifth of that of a **bottle** made from **polyethylene** terephthalate alone. When the **bottle** was let fall repeatedly 10 times, no delamination between the layers was observed.

DETDESC:

DETD(58)

The oxygen permeability of the **bottle** made from **polyethylene** terephthalate along was 15 cc/m.².day.atm. (37.degree. C.).

DETDESC:

DETD(60)

A primary bottomed preform of **polyethylene** terephthalate (inherent viscosity 0.82) having a length of 120 mm, an inside diameter of 25 mm and a side wall. . . with hot air at 90.degree. C. for 2 minutes. The coated preform was then dipped in a solution of an **ethylene-vinyl alcohol** copolymer having a vinyl alcohol content of 72 mole % in a mixture of propanol and water and then dried. . .

DETDESC:

DETD(61)

The . . . to a temperature at which it had elastic deformability. Then, the preform was inserted into an injection mold (core) and **polyethylene** terephthalate having an inherent viscosity of 0.82 was

injected onto the coated surface (outside surface) of the coated preform to. . .

DETDESC:

DETD(62)

The . . . was conditioned to a temperature of about 95.degree. C., and then biaxially stretched and blow-molded to give a stretched multilayer **bottle** having an average body thickness of about 250 microns and an inner capacity of 500 cc.

DETDESC:

DETD(63)

The **bottle** had an oxygen permeability of 2.9 cc/m.².day.atm. (37.degree. C.) which was less than one-fifth of that of a **bottle** made from **polyethylene** terephthalate alone. When the **bottle** was let fall repeatedly 10 times, no delamination between the layers was observed.

DETDESC:

DETD(65)

A primary bottomed preform of **polyethylene** terephthalate (inherent viscosity 0.82) having a length of 120 mm, an inside diameter of 25 mm and a side wall. . . thickness of 1.5 mm was formed by injection molding. The primary preform was then dipped in a solution of an **ethylene-vinyl alcohol** copolymer having a vinyl alcohol content of 72 mole % in a mixture of propanol and water, and dried with. . .

DETDESC:

DETD(66)

The coated preform was inserted into an injection mold, the **polyethylene** terephthalate having an inherent viscosity of 0.82 was injected onto the coated surface (outside surface) of the coated preform to. . .

DETDESC:

DETD(67)

The . . . preform was conditioned to a temperature of 95.degree. C., and then biaxially stretched and blow-molded to give a stretched multilayer **bottle** having an average body thickness of about 250 microns and an inner capacity of 500 cc. But the operability of stretching blow-molding was poor, and the **bottle** had poor transparency.

DETDESC:

DETD(68)

The coated film of this **bottle** was non-uniform, and its oxygen permeability of the **bottle** was 5.8 cc/m.².day.atm. (37.degree. C.).

CLAIMS:

CLMS(1)

What is claimed is:

1. A process for producing a stretched multilayer polyester **bottle** which comprises axially stretching a bottomed multilayer preform comprised of an inside and an outside polyester surface layer and an . . . simultaneously stretching it circumferentially by blowing; wherein said multilayer preform is produced by coating a solution or emulsion of an **ethylene-vinyl alcohol** copolymer on one surface of a primary preform of the polyester molded in advance, drying the coated preform at a temperature at which no whitening owing to the crystallization of the polyester occurs to thereby form a thin but **continuous film** of the **ethylene-vinyl alcohol** polymer on the primary preform, the coated film of the **ethylene-vinyl alcohol** copolymer having such a thickness distribution that its thickness at the bottom portion of the preform is greater than the. . .

CLAIMS:

CLMS (2)

2. The process of claim 1 wherein the **ethylene-vinyl alcohol** copolymer has a vinyl alcohol unit content of 50 to 95 mole %.

CLAIMS:

CLMS (3)

3. The process of claim 1 wherein the coated film of the **ethylene-vinyl alcohol** copolymer has such a thickness distribution that its thickness at the bottom portion of the preform becomes 3 to 15. . .

:4

4. 4,515,836, May 7, 1985, Process for coating substrates with aqueous polymer dispersions; Walter H. Cobbs, Jr., et al., 427/425; 215/12.2; 427/421; 428/36.7, 483 [IMAGE AVAILABLE]

:5

5. 4,573,429, Mar. 4, 1986, Process for coating substrates with aqueous polymer dispersions; Walter H. Cobbs, Jr., et al., 118/322, 320, 326 [IMAGE AVAILABLE]

:6

6. 5,492,953, Feb. 20, 1996, Resin composition; Sumio Itamura, et al., 524/239, 242, 427, 436, 449, 451, 503, 528; 525/60, 61, 240 [IMAGE AVAILABLE]

:ab

US PAT NO: 5,492,953 [IMAGE AVAILABLE]

L6: 6 of 27

ABSTRACT:

Provided are resin compositions comprising the following (A), (B), (C), which is at least one member selected from (C.sub.1) through (C.sub.3) and (D):

(A): a polyolefin,

(B): a saponified product of an ethylene-vinyl acetate copolymer having an ethylene content of 20 to 65 mol % and a saponification degree of vinyl acetate component of at least 96%,

(C): (C.sub.1): at least one inorganic substance selected from titanium oxide, talc, calcium carbonate, mica and absorptive inorganic materials, (C.sub.2): at least one compound selected from the group consisting of metal salts of higher fatty acid having 8 to 22 carbon atoms, metal

salts of ethylenediaminetetraacetic acid and hydrotalcite, and (C.sub.3): a polyolefin modified with an unsaturated carboxylic acid or derivatives thereof;

and,

(D): a saponified product of an ethylene-vinyl acetate copolymer having an ethylene content of 68 to 98 mol % and a saponification degree of vinyl acetate component of at least 20%.

The compositions of the present invention have excellent compatibility within themselves and significantly solve the problems, upon molding, of molding instability such as charred resin on screw, generation of lip stain, pressure increase in extruder, abnormal flow and generation of (turbulence) wavy pattern on the surface of molded articles.

:7

7. 5,389,709, Feb. 14, 1995, Resin composition; Sumio Itamura, et al., 524/239, 242, 427, 436, 449, 451, 503, 528; 525/60, 61, 240 [IMAGE AVAILABLE]

:8

8. 5,196,469, Mar. 23, 1993, **Ethylene/vinyl alcohol** coatings; Virginia P. Cushing, et al., 524/300; 427/407.1, 411, 412.5; 524/321, 389, 522 [IMAGE AVAILABLE]

:ab

US PAT NO: 5,196,469 [IMAGE AVAILABLE]

L6: 8 of 27

ABSTRACT:

A semi-aqueous **ethylene-vinyl alcohol** coating composition that is a stable, homogeneous solution which is capable of being easily applied to a substrate to form a multi-layer structure at room temperature, by spray, rod, gravure, or other mechanical means. Upon evaporation of the volatile components, this coating solution leaves a clear, homogeneous film comprising **EVOH**. The film resists degradation and discoloration during the lifetime of the structure, and upon incineration or recycling does not evolve harmful acids into the environment.

:9

9. 4,771,935, Sep. 20, 1988, Plastic **containers** embodying a peel seal and method of preparing same; Ihab M. Hekal, 229/3.5R; 156/334; 206/484.2; 229/123.1, 125.35 [IMAGE AVAILABLE]

:ab

US PAT NO: 4,771,935 [IMAGE AVAILABLE]

L6: 9 of 27

ABSTRACT:

A polyolefin **container** is disclosed which is hermetically sealed with a complementary lid extending across the open **container** the opposed faces of the **container** surface and the lid being bonded together by a peelable, heat seal layer intermediate between the opposed faces. The heat seal layer is comprised of a mixture of a particulate, filler and first and second polyolefin resins, the second polyolefin resin having a melt flow rate at least about three times greater than the melt flow rate of the first polyolefin resin.

:10

10. 5,062,569, Nov. 5, 1991, Peelably sealed plastic packages and method of preparing same; Ihal M. Hekal, 229/3.5R; 156/334; 206/484; 220/359; 229/125.35 [IMAGE AVAILABLE]

:ab

ABSTRACT:

A polypropylene **container** is disclosed which is hermetically sealed with a complementary lid extending across the open **container** the opposed faces of the **container** surface and the lid being bonded together by a peelable, heat seal layer intermediate between the opposed faces. The heat seal layer is comprised of a mixture of a particulate filler and an olefin polymer blend comprised of a homogeneous mixture of an olefin homopolymer, a highly crystalline propylene-ethylene block copolymer and an elastomeric ethylene-propylene copolymer.

:11

11. 5,498,478, Mar. 12, 1996, **Polyethylene** glycol as a binder material for fibers; Michael R. Hansen, et al., 428/372, 357, 359, 375, 393; 442/417 [IMAGE AVAILABLE]

:12

12. 5,096,738, Mar. 17, 1992, Siloxane polymers and copolymers as barrier, coatings and method of producing barrier coating properties therewith; John E. Wyman, 427/503, 387, 393.4, 393.5; 428/339, 447, 451 [IMAGE AVAILABLE]

:13

13. 5,175,035, Dec. 29, 1992, Multilayer sheet with one layer easily peelable from another; Francis Pinsolle, et al., 428/35.7, 349, 516, 523 [IMAGE AVAILABLE]

:14

14. 5,432,000, Jul. 11, 1995, Binder coated discontinuous fibers with adhered particulate materials; Richard H. Young, Sr., et al., 428/372, 357, 361, 373, 375, 378, 393 [IMAGE AVAILABLE]

:15

15. 4,225,650, Sep. 30, 1980, Crosslinkable polymer powder and laminate; Robert A. van Brederode, et al., 428/405, 407, 429, 447; 525/342, 387 [IMAGE AVAILABLE]

:16

16. 5,701,724, Dec. 30, 1997, Method and apparatus for forming and hermetically sealing slices of food items; Vincent A. Meli, et al., 53/451, 122, 374.5, 477, 551; 426/130, 414 [IMAGE AVAILABLE]

:17

17. 5,667,071, Sep. 16, 1997, Photosensitive material package and packaging apparatus for the same; Isao Nakagoshi, et al., 206/455, 389, 471, 497; 428/34.9 [IMAGE AVAILABLE]

:18

18. 5,440,860, Aug. 15, 1995, Method and apparatus for forming and hermetically sealing slices of food items; Vincent Meli, et al., 53/451, 122, 374.5, 477, 551; 426/130, 414 [IMAGE AVAILABLE]

:19

19. 5,156,900, Oct. 20, 1992, Leather-like sheet materials and method of

producing same; Takeo Nishimura, 428/151; 427/245; 428/315.5, 315.9, 423.3, 904 [IMAGE AVAILABLE]
:20

20. 5,412,016, May 2, 1995, Process for making polymeric inorganic-organic compositions; Kenneth G. Sharp, 524/430, 431, 442; 525/61, 100, 326.2, 329.7, 330.3, 331.5, 342, 389, 431, 446, 903; 528/39 [IMAGE AVAILABLE]
:21

21. 5,102,733, Apr. 7, 1992, Repulpable pressure-sensitive adhesive constructions; Mary E. Zawadzki, 428/343; 162/4; 428/211, 355AC, 355BL [IMAGE AVAILABLE]
:22

22. 5,619,844, Apr. 15, 1997, Method and apparatus for forming a slice of a food item having a heat tacks seal; Vincent A. Meli, et al., 53/550, 371.4, 371.5, 374.3, 374.4; 99/453; 426/410, 414 [IMAGE AVAILABLE]
:23

23. 5,516,585, May 14, 1996, Coated fiber product with adhered super absorbent particles; Richard H. Young, Sr., et al., 428/372, 357, 361, 373, 375, 378, 393; 442/330 [IMAGE AVAILABLE]
:24

24. 5,347,792, Sep. 20, 1994, Method and apparatus for forming a slice of a food item having a heat tack seal; Vincent A. Meli, et al., 53/450, 371.4, 371.5, 374.3, 374.4, 479, 550; 99/453; 426/130, 410, 414 [IMAGE AVAILABLE]
:25

25. 5,230,959, Jul. 27, 1993, Coated fiber product with adhered super absorbent particles; Richard H. Young, Sr., et al., 428/372, 359, 361, 373, 375, 378, 393 [IMAGE AVAILABLE]
:26

26. 5,064,689, Nov. 12, 1991, Method of treating discontinuous fibers; Richard H. Young, Sr., et al., 427/202; 156/62.2; 264/121, 122, 123; 425/83.1 [IMAGE AVAILABLE]
:27

27. 5,057,166, Oct. 15, 1991, Method of treating discontinuous fibers; Richard H. Young, Sr., et al., 156/62.2; 19/305; 156/62.6, 166, 181; 264/121; 425/80.1 [IMAGE AVAILABLE]
:28

27 ANSWERS ARE AVAILABLE. SPECIFIED ANSWER NUMBER EXCEEDS ANSWER SET SIZE

US PAT NO: 4,880,675 [IMAGE AVAILABLE]
TITLE: Hot-fillable plastic **containers**

L10: 2 of 5

ABSTRACT:

The present invention is an improved plastic **container** having both improved thermal resistance and improved aroma and flavor barrier properties. The **container** comprises a **polyethylene** inner layer having a thickness in the range of 0.5 to 10.0 mil, and a coextruded **polypropylene** outer layer having a thickness such that the ratio of **polypropylene** to **polyethylene** is at least 2:1, and wherein the surface of the **polyethylene** layer has been treated with a reactive source of fluorine.

SUMMARY:

BSUM(2)

The present invention relates to plastic **containers** having good barrier properties and temperature resistance, and processes for making the same.

SUMMARY:

BSUM(4)

Preventing scalping of flavor or aroma components into the walls of plastic **containers** is a matter growing concern in the packaging industry. Flavor and aroma components, mostly volatile organics, are typically present at parts per million or even at parts per billion levels. Most common plastics, such as **polyethylene**, **polypropylene**, polystyrene, etc., tend to absorb, entirely or selectively, such volatile organics thereby either distorting or depriving the product of its. . .

SUMMARY:

BSUM(5)

One method of solving this problem has been by modifying the surface of **polyethylene** using fluorination. A number of flavor-sensitive products, however, such as juices, are "hot-filled" or filled at temperatures far above the softening and distortion points for **polyethylene**, thereby making such **containers** unsuitable for these uses.

SUMMARY:

BSUM(6)

Using **polypropylene** for such **containers** is an attractive alternative from cost, strength, and temperature resistance standpoints; however, like **polyethylene**, **polypropylene** also vigorously scalps flavor and aroma components from packaged goods, especially food products. Fluorinating **polypropylene** **containers** has proven to be significantly less successful in preventing the scalping of flavor/aroma components, therefore also making such **containers** undesirable for many applications.

SUMMARY:

BSUM(7)

Joffre, U.S. Pat. No. 2,811,468 teaches a method of imparting barrier properties to **polyethylene** films by fluorinating at least one surface of said film to contain not more than about 3.5% by weight fluorine, . . .

SUMMARY:

BSUM(8)

Dixon, . . . such as sulfur dioxide, carbon monoxide, carbon dioxide, oxygen, chlorine, bromine, etc. can also enhance the physical properties of the **container**.

SUMMARY:

BSUM(9)

Beck, U.S. Pat. No. 4,550,043 discloses preforms for use in blow molding **containers** which are suitable for use in conjunction with hot products which must be subjected to pasteurization. The preform comprises inner. . .

SUMMARY:

BSUM(11)

The present invention is an improved plastic **container** and a method of forming such a **container** by coextruding a multilayer plastic parison or sheets.

SUMMARY:

BSUM(12)

The **container** comprises a **polyethylene** (PE) inner layer having a thickness in the range of 0.5 to 10.0 mil., and a coextruded **polypropylene** (PP) outer layer having a thickness such that the ratio of **polypropylene** to **polyethylene** thickness is at least 2:1, and wherein the surface of the **polyethylene** layer which forms the interior of the **container** has been surface treated with a reactive source of fluorine.

SUMMARY:

BSUM(13)

The **container**, comprising a coextruded **polyethylene** interior and **polypropylene** exterior, is formed by coextruding thermoplastic PP/PE followed by blow-molding, injection molding, thermoforming and the like, into the desired shape. The surface of the PE layer which forms the interior of the **container** is treated with a reactive source of fluorine, either during the molding process or after the **container** is formed. The reactive source of fluorine can be any suitable source, such as fluorine containing liquid or plasma, but. . .

SUMMARY:

BSUM(14)

The resultant **containers** have high thermal resistance, and also high flavor and aroma barrier properties.

DETDESC:

DETD(2)

The present invention is a **container** having both improved thermal resistance and improved flavor and aroma barrier properties. The **container** comprises a **polyethylene** inner layer having a thickness in the range of 0.5-10.0 mil, and coextruded **polypropylene** outer layer having a thickness such that the ratio of **polypropylene** to **polyethylene** thickness is at least 2:1. Although the extrudate and a significant portion of the resultant **container** have a **polypropylene/polyethylene** thickness ratio of at least 2:1, due to varied flow rates of the two polymers, the resultant **container** may have areas wherein the ratio drops below this level. The **polyethylene** inner layer which forms the interior of the **container** has been surface treated with a reactive source of fluorine. The interior **fluorinated polyethylene** layer imparts the **container** with good flavor/aroma barrier properties while the **polypropylene** outer layer acts as the structural layer, providing the necessary thermal resistance to prevent deformation of the **container** at hot-fill temperatures; typically around 180.degree.-205.degree. F. The **polypropylene** outer layer includes homopolymers and/or copolymers of **polypropylene**.

DETDESC:

DETD(3)

The **containers** of the present invention exhibit properties which cannot be achieved by using **polyethylene** or **polypropylene** alone, since **polyethylene** cannot withstand "hot-fill" temperatures, and **polypropylene**, even when fluorinated, was found not to provide good barrier properties. Reversing the layers such that the **polypropylene** is the interior layer with the treated **polyethylene** the outer layer is ineffective since flavor and aroma components are lost due to migration into the **polypropylene**. It has been found that only **containers** having the structure as set out in the present invention are suitable for "hot-fill" applications when flavor and/or aroma preservation are important. Surprisingly, when each layer is within the thickness ranges set out above, the interior **polyethylene** layer will not deform or delaminate from the **polypropylene** layer, even when subjected to "hot-fill" temperatures well above the softening and distortion point of **polyethylene**. If the thickness of either layer is outside of the above prescribed limits there is a good chance of delamination between the layers or deformation of the **container**.

DETDESC:

DETD(4)

In . . . optional embodiment of the present invention, a tie layer, such as a copolymer of maleic anhydride with ethylene vinylacetate (EVA), **polypropylene**, **polyethylene**, etc., may be present between the **polypropylene** outer layer and the **polyethylene** inner layer to enhance the adhesion between the two layers. In addition to such a tie layer, an oxygen barrier layer may be coextruded between the **polypropylene** and **polyethylene** layers. Examples of such possible oxygen barrier layers included: **polyethylene** vinyl alcohol, polyvinylidene chloride, nylons, and the like.

DETDESC:

DETD(5)

The surface of the interior **polyethylene** layer which forms the

interior of the **container** is fluorinated to a sufficient degree to impart flavor and aroma barrier properties. The extent to which such a surface. . . .

DETDESC:

DET D(6)

The **containers** of the present invention are formed by molding a thermoplastic multilayer extrudate comprising a **polyethylene** inner layer and a **polypropylene** outer layer having thickness as set out above. The multilayer extrudate can be molded into **containers** by a variety of methods, such as by blow molding, thermoforming, injection molding, or any other suitable method. The inner **polyethylene** layer forms the interior of the **container**, and the **polypropylene** layer forms the exterior wall of the **container**. The surface of the **polyethylene** layer which forms the interior of the **container** is treated with a reactive source of fluorine to impart flavor and aroma barrier properties. The **polyethylene** surface can be treated during the molding process, or may be post-treated after the **container** is formed. Any suitable reactive source of fluorine can be used, including fluorine-containing plasmas, fluorine-containing gas streams, fluorine dissolved in. . . . the like. In most embodiments it is preferred to use a fluorine-containing gas stream, and in the case where the **containers** are formed by blow molding, employing the fluorine stream directly as the blowing gas is preferred. The fluorine-containing gas stream. . . .

DETDESC:

DET D(7)

Optionally, the multilayer extrudate may have a tie layer positioned between the **polypropylene** and **polyethylene** layers to enhance adhesion of the layers. Additionally, one or more other layers, such as an oxygen barrier layer may. . . . only requirement being that such layers do not have a significant detrimental effect on the desired properties of the resultant **container**.

DETDESC:

DET D(8)

After the **container** is formed, any number of other treatments or additions can be performed, such as applying oxygen barrier coating to either the interior or exterior of the **container** or both.

DETDESC:

DET D(11)

The tests described in the examples below were carried out on various 16-oz round blow-molded **containers**. The compositions of the various **containers** were as follows:

DETDESC:

DET D(12)

(a) untreated high density **polyethylene** (control HDPE)

DETDESC:

DET D(13)

(b) untreated **polypropylene** (control PP)

DETDESC:

DETD(15)

(d) coextruded **container** with internal HDPE layer and external PP layer (Coex PE/PP), either fluorinated or untreated.

DETDESC:

DETD(17)

Samples of each of the **containers** described above (except fluorinated Coex PE/PP) were filled with boiling water at (100.degree. C.) and capped. Both the untreated and fluorinated HDPE **containers** paneled (deformed) readily, whereas the untreated PP, fluorinated PP and Coex PE/PP **containers** showed no deformation. These results are summarized in Table 1 below.

DETDESC:

DETD(18)

TABLE 1

Container	Condition
Control HDPE	Severely deformed
Fluorinated HDPE	Severely deformed
Control PP	No deformation
Fluorinated PP	No deformation
Coextruded HDPE-PP.	.. .

DETDESC:

DETD(19)

The results above demonstrate that, while both fluorinated and unfluorinated HDPE **container** severely deform under high temperatures, the coextruded **containers** with HDPE inner and PP outer layers easily sustained hot-fill temperatures.

DETDESC:

DETD(21)

Samples of each of the **containers** described above were filled with toluene and stored in an oven at 50.degree. C. for 4 weeks. Weight losses for the **containers** were measured after the 4 week storage period and are reported in Table 2 below.

DETDESC:

DETD(22)

TABLE 2

Bottle	% wt. Loss (4 wks. @ 50.degree. C.)
Control HDPE	19.4
Fluorinated HDPE	0.4
Control PP	99.8
Fluorinated PP	85.1
Int. Fluorinated.	.. .

DETDESC:

DETD(23)

The results reported in Table 2 above clearly show that the internal fluorinated Coex PE/PP **container** exhibits excellent barrier properties for organics such as toluene, even under elevated temperatures.

DETDESC:

DETD(25)

Runs were carried out to determine the flavor barrier properties and thermal resistance of samples of the above **containers**, compared to the properties which are generally known for conventional glass **containers**. Several of the **containers** described above were filled with hot (about 82.degree. C.) aqueous solution containing 0.1% methanol and 100 ppm limonene, and were . . . important flavor ingredient in a variety of juices, especially orange juice. Samples of the aqueous solution were taken from the **containers** shortly after they were filled and also after a 4 week period. The results are reported in Table 3 below.

DETDESC:

DETD(26)

TABLE 3

Container	Limonene	
	Container Condition	Concentra- tion (ppm)
	After 15 mins.	After 4 weeks
Glass	(visually unchanged)	
		N.C..sup.(1)
HDPE control	(severely deformed)	0
HDPE Fluorinated.	. . .	= No Significant Change. Data was not actually obtained for these runs, however it is well known that conventional glass containers are well suited for this type of application, and previous testing also proved the thermal resistance and barrier properties of the Coex HDPE/PP container .
	.sup.(2)	Analytical method did not give a precise measurement, although relative concentrations could be measured.

HDPE Fluorinated. . . = No Significant Change. Data was not actually obtained for these runs, however it is well known that conventional glass **containers** are well suited for this type of application, and previous testing also proved the thermal resistance and barrier properties of the Coex HDPE/PP **container**.
.sup.(2) Analytical method did not give a precise measurement, although relative concentrations could be measured.

DETDESC:

DETD(27)

The results above indicate the fluorinated Coex PE/PP **container** would be expected to retain its structure under the hot-fill conditions, and also exhibit excellent flavor barrier properties, even over a 4 week period, while all the other plastic **containers** tested proved unsuitable for this type of application. Consequently, of the samples listed above, only the fluorinated Coex PE/PP **container** would be a suitable substitute for conventional glass **containers**.

CLAIMS:

CLMS(1)

What is claimed is:

1. A coextruded **container** having both improved thermal resistance and improved flavor and aroma barrier properties comprising: a **polyethylene** inner layer having a thickness in the range of 0.5-10.0 mil which forms the interior surface of the **container**, and a **polypropylene** outer layer which forms the exterior surface of the **container**, said **polypropylene** layer having a thickness such that the ratio of **polypropylene** to **polyethylene** thickness is at least 2:1, and wherein said **polyethylene** layer which forms the interior surface of the **container** has been treated with a reactive source of fluorine.

CLAIMS:

CLMS (2)

2. A **container** in accordance with claim 1 wherein a tie layer is present between the **polypropylene** and **polyethylene** layer to enhance adhesion between the two layers

CLAIMS:

CLMS (3)

3. A **container** in accordance with claim 1 which comprises an oxygen barrier layer between the **polypropylene** and **polyethylene** layers.

CLAIMS:

CLMS (4)

4. A **container** in accordance with claim 3 wherein said oxygen barrier layer is selected from the group consisting of **ethylene vinyl alcohol**, polyvinylidene chloride, nylon, and mixtures thereof.

CLAIMS:

CLMS (5)

5. A **container** in accordance with claim 1 wherein a tie layer in combination with an oxygen barrier layer is positioned between the **polyethylene** and **polypropylene** layers.

CLAIMS:

CLMS (6)

6. A **container** in accordance with claim 1 further comprises a tie layer in combination with an oxygen barrier layer is located on the surface of the **polypropylene** layer which forms the exterior of the **container**.

CLAIMS:

CLMS (7)

7. A **container** in accordance with claim 1 wherein said **container** was blow molded from a **polypropylene/polyethylene** multilayer extrudate preform.

CLAIMS:

CLMS (8)

8. A **container** in accordance with claim 1 wherein said **container**

was formed by a thermoforming or injection-molding process.

CLAIMS:

CLMS (9)

9. A **container** in accordance with claim 1 which has been coated with an oxygen barrier coating.

CLAIMS:

CLMS (10)

10. A **container** in accordance with claim 1 in which the exterior surface can be hot-filled with liquids at temperatures up to 205. degree..

CLAIMS:

CLMS (11)

11. A **container** in accordance with claim 1 wherein the interior surface has been treated with a reactive source of gaseous fluorine comprising. . .

CLAIMS:

CLMS (12)

12. In a process for forming a **container** by molding a thermoplastic material, the improvement for increasing the thermal resistance and flavor and aroma barrier properties, which comprises: molding said **container** using a coextruded thermoplastic multilayer material comprising a **polyethylene** inner layer having a thickness in the range of 0.5-10.0 mil and a **polypropylene** outer layer having a thickness such that the ratio of **polypropylene** to **polyethylene** thickness is at least 2:1, such that the **polyethylene** layer forms the interior wall of the **container**, and surface treating the interior **polyethylene** layer with a reactive source of fluorine.

CLAIMS:

CLMS (13)

13. A process in accordance with claim 12 wherein said thermoplastic multilayer material has a tie layer positioned between the **polypropylene** and **polyethylene** layers to enhance adhesion between the layers.

CLAIMS:

CLMS (14)

14. A process in accordance with claim 12 wherein said thermoplastic multilayer material has an oxygen barrier layer between the **polypropylene** and **polyethylene** layers.

CLAIMS:

CLMS (15)

15. A process in accordance with claim 14 wherein said oxygen barrier layer is selected from the group consisting of **polyethylene** vinyl alcohol, polyvinylidene chloride, nylons, and mixtures thereof.

CLAIMS:

CLMS (16)

16. A process in accordance with claim 12 wherein said **container** is formed by blow molding said coextruded thermoplastic multilayer material.

CLAIMS:

CLMS (17)

17. A process in accordance with claim 16 wherein said interior surface of the **polyethylene** layer is treated with a reactive source of fluorine during the blow molding process by using a fluorine-containing gas stream.

CLAIMS:

CLMS (19)

19. A process in accordance with claim 12 wherein said **container** is formed by a thermoforming or injection-molding process.

CLAIMS:

CLMS (20)

20. A process in accordance with claim 12 wherein said interior **polyethylene** layer is post-treated with a reactive source of fluorine.

:3

3. 5,165,990, Nov. 24, 1992, Stampable sheet; Akikazu Nakano, 428/297.4, 132, 136; 442/136; 525/132 [IMAGE AVAILABLE]
:ab

US PAT NO: 5,165,990 [IMAGE AVAILABLE] L10: 3 of 5

ABSTRACT:

A stampable sheet which comprises 95 to 20% by weight of styrene polymer having a syndiotactic configuration (a) and 5 to 80% by weight of fibrous reinforcing material having an average fiber length of at least 1 mm (b) which is excellent in heat resistance, impact resistance, dimensional stability and dielectric properties is disclosed.

:4

4. 5,412,024, May 2, 1995, Thermoplastic resin composition; Akihiko Okada, et al., 524/577, 494, 496, 578; 525/333.3 [IMAGE AVAILABLE]
:ab

US PAT NO: 5,412,024 [IMAGE AVAILABLE] L10: 4 of 5

ABSTRACT:

There is disclosed a thermoplastic resin composition which comprises a terminal-modified styrenic polymer having syndiotactic configuration the terminal of which is bonded to a compound having a polar group or a composition of the above terminal-modified styrenic polymer and a terminal-unmodified styrenic polymer having syndiotactic configuration, and an inorganic filler. The composition of the present invention is excellent in resistances to water, impact and heat as well as in mechanical properties and adhesivity with inorganic fillers without impairing the crystallization of the styrenic polymer having syndiotactic configuration.

5. 4,933,526, Jun. 12, 1990, Shaped microwaveable food package; John R. Fisher, et al., 219/730; 99/372, DIG.14; 219/759; 426/107, 234, 243
[IMAGE AVAILABLE]
:ab

US PAT NO: 4,933,526 [IMAGE AVAILABLE]

L10: 5 of 5

ABSTRACT:

The present invention provides a package suitable for microwave cooking and browning of food items, comprising a microwave susceptive mold containing at least one cavity for containing food items, and a microwave susceptive cover extending over and closing the cavities.

:kwic

US PAT NO: 4,933,526 [IMAGE AVAILABLE]

L10: 5 of 5

SUMMARY:

BSUM(9)

Copending . . . couples to both the electrical and magnetic components of the microwave field. One such film comprises stainless steel sputtered onto **polyethylene** terephthalate film.

SUMMARY:

BSUM(11)

It . . . of appropriate texture and appearance. For example, uniform reconstituted potato chips are sold commercially, nested and packed in a compact **container**. It is believed that for formation of such potato chips, a dehydrated potato powder is hydrated and conventionally baked in. . .

DETDESC:

DETD(4)

The . . . for use in a microwave oven. Examples of suitable materials include, paperboard, glass, and many types of plastic, including crystallized **polyethylene** terephthalate (CPET), aliphatic crystalline grades of nylon, thermosetting polyester, **polypropylene**, polycarbonate, polyetherimide, and high impact polystyrene. The tray may also be made of laminated structures, for example, an engineering polymer such as **polypropylene**, polycarbonate, or polyetherimide laminated with **ethylene vinyl alcohol** copolymer, polyamide, or polyvinylidene chloride. Polymeric compositions containing various fillers or reinforcing agents such as glass, mica, talc, calcium carbonate, . . .

DETDESC:

DETD(6)

The . . . be encountered under microwave cooking conditions, so the film should maintain its integrity at such temperatures. Certain polyesters, such as **polyethylene** terephthalate (PET), having a melting point of about 260.degree. C., are particularly suitable for this purpose. Other suitable materials may include certain types of polyesters, polyamides, cellophane, cellulose triacetate, ethylene chlorotrifluoroethylene copolymers, **fluorinated polyethylene**,

polyimides, polysulfones, polyvinyl alcohol polymers, polyetheretherketones, polytetrafluoroethylene, and others.

DETDESC:

DETD(12)

It . . . laminated structure provides a limited, controlled amount of shrinkage to the film. Particularly preferred for this layer is heat stabilized **polyethylene** terephthalate. Heat stabilized PET is made from a regular grade of PET film by a stabilization process involving a series. . . .

DETDESC:

DETD(17)

A . . . mm wide, having a triangular cross section.) The mold was made of cardboard, and was lined with a film of **polyethylene** terephthalate coated with a thin layer of aluminum flakes embedded in a low-melting polyester matrix, as described in more detail. . . .

08/917044 04/20/98

(FILE 'USPAT' ENTERED AT 14:50:50 ON 20 APR 1998)

L1 172 S (RECYCL? OR PCR) AND (POLYETHYLENE AND PE) AND (POLYPROP
YLE

L2 282659 S BOTTLE OR CONTAINER

L3 121 S L1 AND L2

L4 1393582 S CONTINU? OR ?UNIFORM?

L5 118 S L3 AND L4

L6 10839 S (CONTINUOUS OR UNIFORM) (W) FILM

L7 2 S L3 AND L6

L8 19875 S RECYCLE? PLASTIC OR SCRAP

L9 45 S (POLYETHYLENE OR PE) AND ((CONTINUOUS OR UNIFORM) (W) (P
OLY

L10 3 S L9 AND L8

L11 6 S L9 AND L2

L12 6 FOCUS L11 1-

L13 47 S L1 AND L8

L14 42 S L13 AND L2

L15 41 S L14 AND L4

L16 41 FOCUS L15 1-

L17 18 S MULTILAYER? (P) RECYCL? (P) PLASTIC (P) (CONTAINER OR BO
TTL

L18 234305 S FLUORIN? POLYETHYLENE OR POLYETHYLENE OR POLYPROPYLENE

L19 18 S L18 AND L17

L20 18 FOCUS L19 1-